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SERDP and ESTCP Technical Exchange Meeting on DoD Operational Range Assessment and Management Approaches

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14. ABSTRACT
This report summarizes the results of a technical exchange meeting sponsored by the Department of Defenses (DoD) Strategic Environmental Research and Development Program (SERDP) and Environmental Security Technology Certification Program (ESTCP) that sought to inform representatives from the range management and assessment communities of applicable technologies developed by SERDP, ESTCP, and the Army Environmental Quality Technology (EQT) Program and to determine the technology needs of the range management and assessment community that could be addressed through additional research and development efforts supported by SERDP and ESTCP.

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LIST OF ACRONYMS

2-D	two-dimensional
AAP	Army Ammunition Plant
AFB	Air Force Base
AFCEE	Air Force Center for Engineering and the Environment
AOC	area of concern
ARAMS	Adaptive Risk Assessment Modeling System™
BDU	Bomb Dummy Unit
BMP	best management practice
CEC	cation exchange capacity
CL-20	China Lake-20
COC	contaminant of concern
CRREL	Cold Regions Research and Engineering Laboratory
CSM	conceptual site model
DNT	dinitrotoluene
DoD	Department of Defense
DQO	data quality objective
Eco-SSL	ecological soil screening level
EL	Environmental Laboratory
EOD	explosive ordnance disposal
EQT	Environmental Quality Technology
ERDC	Engineer Research and Development Center
ESTCP	Environmental Security Technology Certification Program
FAV	Final Acute Value
FY	fiscal year
g	gram(s)
GIS	geographic information system
HMX	octahydro-1,3,5,7-tetranitro-1,3,5,7 tetrazocine
I&E	Installations & Environment
IRIS	Integrated Risk Information System
ITAM	Integrated Training Area Management
ITRC	Interstate Technology Regulatory Council
K_d	soil-water partition coefficient
K_{ow}	octanol-water partition coefficient
kg	kilogram(s)
L	liter
LAW	light anti-tank weapon
LOAEL	lowest observed adverse effect level

m	meter(s)
MANG	Massachusetts Army National Guard
MC	munitions constituent
μg	microgram(s)
M	million
mg	milligram(s)
MIDAS	Munitions Items Disposition Action System
mm	millimeter(s)
MMR	Massachusetts Military Reservation
MMRP	Military Munitions Response Program
MNA	monitored natural attenuation
NAS	National Academies of Science
NC	nitrocellulose
NG	nitroglycerin
NOAEL	no observed adverse effect level
NQ	nitroguanidine
NRC	National Research Council
OASN	Office of the Assistant Secretary of the Navy
OB/OD	open burn/open detonation
ODUSD	Office of the Deputy Under Secretary of Defense
ORAP	Operational Range Assessment Program
PETN	pentaerythritol tetranitrate
PRB	permeable reactive barrier
QA/QC	quality assurance/quality control
RDT&E	research, development, testing, and evaluation
RDX	1,3,5-hexahydro-1,3,5-trinitrotriazine
REVA	Range Environmental Vulnerability Assessment
RSEPA	Range Sustainability Environmental Program Assessment
SERDP	Strategic Environmental Research and Development Program
SRO	Sustainable Range Oversight
s/s	solid/solution
TNT	2,4,6-trinitrotoluene
TRI	Toxic Release Inventory
UCL	upper confidence limit
USACE	U.S. Army Corps of Engineers
USAEC	U.S. Army Environmental Command
USAF	U.S. Air Force
USEPA	U.S. Environmental Protection Agency
UXO	unexploded ordnance
XAS	x-ray absorption spectroscopy

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This report summarizes the results of a technical exchange meeting sponsored by the Department of Defense's (DoD) Strategic Environmental Research and Development Program (SERDP) and Environmental Security Technology Certification Program (ESTCP) that sought to inform representatives from the range management and assessment communities of applicable technologies developed by SERDP, ESTCP, and the Army Environmental Quality Technology (EQT) Program and to determine the technology needs of the range management and assessment community that could be addressed through additional research and development efforts supported by SERDP and ESTCP. A steering committee composed of Dr. John Cullinane, U.S. Army Corps of Engineers (USACE) Engineer Research and Development Center (ERDC)-Environmental Laboratory (EL); Mr. Michael Dette, U.S. Army Environmental Command (USAEC); Ms. Wanda Holmes, Chief of Naval Operations, N45; Dr. Tom Jenkins, USACE ERDC-Cold Regions Research and Engineering Laboratory (CRREL); Dr. Jeffrey Marqusee (SERDP/ESTCP); Ms. Emily McBride, Booz Allen Hamilton; Ms. Deborah Morefield, Office of the Assistant Secretary of the Navy (OASN) Installations and Environment (I&E); and Ms. Jennifer Simmons, HQ Marine Corps, assisted SERDP and ESTCP in defining the scope of the meeting and determining the meeting format.

To communicate the state of the science regarding the assessment and management of operational ranges, background papers were authored and presented by Dr. Jenkins and Dr. Steve Larson, USACE ERDC-EL. These background papers established the foundation for discussions at the meeting as well as sections of this final report. The background papers are provided in Appendix B.

Breakout group discussions to identify and prioritize gaps in knowledge and technology were led by Dr. Jenkins; Mr. Andrew Rak, Noblis; and Dr. Rob Steffan, Shaw Environmental, Inc. Discussions were documented by rapporteurs, including Mr. Andy Martin, USACE ERDC-EL; Ms. Alicia Shepard, HydroGeoLogic, Inc.; and Ms. Catherine Vogel, Noblis. These rapporteurs then integrated their notes and authored significant sections of the final report.

Within SERDP and ESTCP, Dr. Jeff Marqusee, Mr. Brad Smith, and Dr. Andrea Leeson provided leadership in the conception and implementation of this technical exchange meeting. Ms. Vogel was instrumental in the development of the meeting. Ms. Sarah Hunt, Ms. Veronica Rice, Ms. Deanne Rider, Ms. Eve Rogers, and Ms. Shepard from HydroGeoLogic, Inc. facilitated all developmental activities for the meeting.

Most importantly, we acknowledge the input of all meeting participants that has resulted in a prioritized list of requirements to guide investments in the areas of operational range assessment and management over the next five to ten years by SERDP and ESTCP. A list of the participants is provided in Appendix A.

EXECUTIVE SUMMARY

The readiness of the military forces depends on their ability to develop and test improved weapons systems and to train troops under realistic operational and wartime scenarios. Therefore, the sustainability of the Department of Defense's (DoD) operational ranges is crucial to allow mission-critical testing and training activities to continue. Concern over the release of munitions constituents (MC) on ranges and the potential for the MCs to migrate to off-range areas is increasing, however, and endangers the long-term sustainability of ranges. DoD policy requires that all DoD ranges and operating areas be managed and operated in such a way as to support their long-term viability and utility to meet the national defense mission while protecting human health and the environment (DoD Directive 3200.15[1]). In support of this policy, all DoD Components are required to establish and implement procedures to assess the environmental impacts of munitions use on operational ranges (DoD Directive 4715.11[2] and DoD Instruction 4715.14[3]). All DoD Components have developed and are currently implementing operational range assessment programs (ORAP).[4]

Over the past several years, the Strategic Environmental Research and Development Program (SERDP), Environmental Security Technology Certification Program (ESTCP), and Army Environmental Quality Technology (EQT) Program have funded a significant body of basic and applied research to gain a better understanding of the MCs resulting from military training activities on ranges and to develop better sampling methodologies applicable for ranges, as well as technologies to treat or contain MCs in soil and groundwater. The results from these efforts are contained in numerous technical reports and papers but have not been integrated into standard or traditional environmental practice. In addition, there are no standards of practice universally accepted by the Services or the regulatory community for conducting range assessments or instituting potential management strategies.

SERDP and ESTCP convened a Technical Exchange Meeting on DoD Operational Range Assessment and Management Approaches on 7–8 August 2007, in Annapolis, Maryland. The objectives of this meeting were to (1) inform representatives from the range management and assessment communities of applicable technologies developed by SERDP, ESTCP, and the Army EQT Program and (2) identify technology needs of the range management and assessment community that could be addressed through additional research and development efforts supported by SERDP and ESTCP. Seventy-five experts—including DoD range managers, DoD range assessment program managers, contractors conducting or designing range assessments, and researchers—participated (Appendix A: Attendee List).

Two breakout sessions—each with three working groups—facilitated discussions of the current state of the science for range assessment and management and identified data gaps that could be addressed through additional research, development, testing, and evaluation (RDT&E) activities. In the first breakout session, participants reviewed current range assessment practices and

[1] http://www.dtic.mil/whs/directives/corres/pdf/320015p.pdf.
[2] http://www.dtic.mil/whs/directives/corres/pdf/471511p.pdf.
[3] http://www.dtic.mil/whs/directives/corres/pdf/471514p.pdf.
[4] Note that each of the DoD Components has a different name for their ORAP: Air Force Operational Range Assessment Plan (ORAP); Army Operational Range Assessment Program (ORAP); Marine Corps Range Environmental Vulnerability Assessment (REVA); and Navy Range Sustainability Environmental Program Assessment (RSEPA).

identified technical issues. The second breakout session focused on identifying technology needs that could be addressed through additional research and development efforts by SERDP and ESTCP in the areas of (1) characterization; (2) risk, modeling, and assessment; and (3) mitigation and management.

Although the state of understanding regarding the release of MCs and their fate and transport in the environment has improved in recent years, it is clear that much remains unknown and that an integrated approach to addressing these data gaps is required. There is a need for sound science and effective tools to assess and manage operational ranges in a manner that reduces risk to human health and the environment. Furthermore, improvements in mitigation technologies and long-term sustainable management approaches are needed. SERDP and ESTCP—as DoD programs that promote the development and demonstration of innovative, cost-effective environmental technologies—must determine how their limited funds can be best invested to improve DoD's ability to assess and mitigate existing risks and reduce future harmful environmental impacts from range usage.

The overarching themes that emerged from the discussions are listed below. In this list, no priority is implied by the order of the listing.

1. **Lack of quantitative data to aid in source term identification and quantification.** This key data gap limits the utility of predictive modeling to determine how and how quickly MCs will migrate in the environment.

2. **Transition and implementation of improved soil sampling strategies.** Much effort has been placed on developing improved soil sampling strategies; however, additional outreach is needed to transition such strategies to the user community and to support strategy implementation.

3. **Improved tools and methodologies to monitor surface water bodies and groundwater.** Much research has been conducted on monitoring energetic compound transformation in terrestrial and groundwater systems; however, research is needed to develop characterization approaches and protocols for effectively assessing the risk posed by MCs in open water bodies. Additionally, effort is needed to develop cost-effective sentinel systems for the *in situ* low-level detection of MCs in groundwater.

4. **Improved understanding of fate and transport parameters for MCs under varying environmental and soil conditions.** An improved understanding of the dissolution and partitioning between the soil and aqueous phases is needed in addition to additional research on the fate and transport of MCs in the vadose zone.

5. **Development of additional toxicity data and ecological soil screening levels (Eco-SSLs) for MCs.** The need for additional toxicity data (acute and chronic) and the development of Eco-SSLs for many of the MCs expected to be found on ranges was identified as a critical need because many of the benchmarks used to define acceptable and unacceptable risk are toxicity based.

6. **Improved predictive modeling capabilities.** Improved predictive modeling capabilities to predict source zone strength and fate and transport of the MCs in the environment are needed. Advancements in this area would allow for quantitative predictions of the release and migration of MCs to be considered during the development of design, use, and long-term management strategies for ranges.

7. **Improved mitigation and long-term management strategies for ranges.** Effort is needed to evaluate the applicability of small arms range management strategies to other types of ranges. Additional effort is warranted to develop long-term sustainable management and mitigation strategies for larger ranges (e.g., air-to-ground, artillery).

Specific research paths and demonstrations were identified by the three working groups and prioritized as either critical or high priority, largely based on the sequence of events required to impact the assessment, mitigation, or management of operational ranges (see Table 1).

The identification of these research and demonstration needs by the technical exchange meeting participants will guide investments by SERDP and ESTCP in the areas of assessment, mitigation, and management of operational ranges over the next five to ten years.

Table 1. Critical and High Priority Research and Demonstration Needs Identified

Characterization Working Group	
Research Needs	
Critical Priority	**High Priority**
Development of Characterization Approaches for Assessing Risk Posed by Munitions Constituents in Water Ranges	Assess Potential of Bag Burning Operations and Use Of Spotting Charges to Generate Contaminant Source Zones
Source Zone Detection and Characterization Techniques	Improved Understanding of the Frequency of Unexploded Ordnance Rupture by Incoming Rounds
Sentinel Monitoring Techniques for Early Warning of Potential Receptor Impact Risk	Improved Understanding of and Sampling Methods to Determine the Mechanisms Controlling Munition Constituent Concentrations in Surface Water
Development of Improved Fate and Transport Parameter Values for Munitions Constituents	Development of Analytical Methods for Future Munitions Constituents
Demonstration Needs	
Critical Priority	**High Priority**
Improved Methods for Developing Conceptual Site Models and Applying Data Quality Objectives for Water Ranges	Improved Source Zone Estimation Techniques Not Dependant Upon Site Sampling
Development of Decision Guidelines for Optimizing Groundwater Well Placement on Operational Ranges	Integration of Multi-Increment Sampling into the Triad Approach
	Development of Early Warning Mechanisms to Inform Sustainable Range Management Decisions
	Development of Munition Constituent Performance Standards for Quality Assurance/Quality Control at Analytical Laboratories
Risk, Modeling, and Assessment Working Group	
Research Needs	
Critical Priority	**High Priority**
Improved Understanding of the Role of Valence State in the Fate, Transport, and Toxicity of Heavy Metals Associated with Munitions Constituents	Development of Structured Process to Evaluate Quality of Existing Toxicity Data
Development of Analytical Methods for Munitions Constituents	Determination of Fate and Transport Parameters for Munitions Constituents in Varying Soil Types
Development of Toxicity Data for Munition Constituents and Munition Constituent By-Products	Development of Terrestrial Toxicity-Based (Chronic and Acute) Screening Benchmarks

Improved Understanding of the Fate and Transport Properties of Munitions Constituents as Military Grade Mixtures	Development of Aquatic Toxicity Data Sets for Munition Constituents to Support Development of Water Quality Criteria
Development of Methodologies and Tools to Determine the Toxicity of Mixtures of Munition Constituents	Development of Methodology to Select Representative Species as Indicators of Ecological Risk at Operational Ranges
	Develop Improved Understanding of the Bioavailability of Munition-Related Heavy Metals in Terrestrial, Freshwater and Marine Environments
	Evaluation of Potential Release of Munition Constituents from Firing Points Located Near Installation Boundaries
Demonstration Needs	
Critical Priority	**High Priority**
Development of Online Human Health and Ecological Toxicity Databases Including Data Quality Descriptors and Information on Benchmark Derivation	Validation of Existing Dissolution Models for Metals
Validate Existing Spatially Explicit Exposure Assessment Models Using a Variety of Receptor Types	Compilation of Data on Munition Items Currently Not Included in the MIDAS
Development of an Improved Understanding of Lead Bioavailability Based on Speciation	Development of Guidance for Appropriate Application of Multi-Increment Sampling Methodology for Ranges
	Development and Demonstration of Forecasting Models to Predict Acceptable Munition Constituent Loading on Ranges
	Validation of Existing Fate, Transport, Exposure, and Toxicity Models to Include Identification of Advantages and/or Limitations
Mitigation and Management Working Group	
Research Needs	
Critical Priority	**High Priority**
Development of Sustainment Approaches to Immobilize or Transform Propellant Constituents Near Firing Points on Small Arms Ranges	Development of Novel Treatment Additives and/or Delivery Methods for Groundwater Treatment and Improved Modeling Capability to Predict Treatment Effectiveness
Development of Innovative, Wide-Area, Near-Surface Soil Treatment Methods for Impact Areas	Improved Best Management Practices for Disposal of Excess Propellant Bags
Development of Alternative Explosives to Replace RDX in Testing and Training Munitions and Explosives	Improvements in Munition Manufacturing, Storage, Transport, and/or Deployment Processes to Eliminate or Decrease Dud Rates
Development of Remote Sensing/Early Warning Monitoring Tools for Detection of Groundwater and Soil Contamination	
Demonstration Needs	
Critical Priority	**High Priority**
Development of Phytostabilization/Phytoremediation Growing Guides for Varying Geographic and Range Use Conditions	Development of Guidance for Transition of Small Arms Range Mitigation/Management Approaches to Single-Site Explosive Ranges
Development of Improved Guidelines for Small Arms Range Chemical Stabilization Technologies	
Improved Storage, Inspection, and Disposition Procedures for Range Clearance Residue	

1 INTRODUCTION

The Strategic Environmental Research and Development Program (SERDP[5]) and Environmental Security Technology Certification Program (ESTCP[6]) are Department of Defense (DoD) programs designed to support research, development, demonstration, and transition of environmental technologies required by the DoD to perform its mission. Assessment and sustainment of testing and training ranges are areas of emphasis for both programs.

1.1 Department of Defense Operational Ranges

DoD policy requires that all DoD ranges and operating areas be managed and operated in such a way as to support their long-term viability and utility to meet the national defense mission while protecting human health and the environment. Environmental considerations that may influence current or future range and operating area activities must be identified as part of the range-sustainment management program (DoD Directive 3200.15[7]). In support of this policy, all DoD Components are required to establish and implement procedures to assess the environmental impacts of munitions use on operational ranges (DoD Directive 4715.11[8] and DoD Instruction 4715.14[9]). All DoD Components have developed and are currently implementing operational range assessment programs (ORAP).[10]

Key elements of the ORAPs include: (1) addressing all operational ranges/range complexes within the United States; (2) using the U.S. Environmental Protection Agency's (USEPA) conceptual site model (CSM) and data quality objectives (DQO) processes; (3) leveraging existing information to the greatest extent possible; (4) reporting and addressing (under the Defense Environmental Restoration Program in accordance with the National Contingency Plan) off-range munitions constituent (MC) migration posing an unacceptable risk requiring mitigation; and (5) periodically (e.g., at least every five years) reevaluating the ranges.

ORAPs must include (1) an inventory of operational ranges; (2) a list of MCs of concern; (3) procedures used to identify sources, pathways, and receptors; (4) procedures used to determine if there is a release or substantive threat of a release of MCs from an operational range to an off-range area that creates an unacceptable risk; (5) procedures for external and internal communication; and (6) following initial assessment, plans for periodic reevaluation. DoD's goal is to assess the potential hazards from off-range migration of MCs and begin any required remediation by fiscal year (FY) 2008.

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[5] http://www.serdp.org/.
[6] http://www.estcp.org/.
[7] http://www.dtic.mil/whs/directives/corres/pdf/320015p.pdf.
[8] http://www.dtic.mil/whs/directives/corres/pdf/471511p.pdf.
[9] http://www.dtic.mil/whs/directives/corres/pdf/471514p.pdf.
[10] Note that each of the DoD Components has a different name for their ORAP: Air Force Operational Range Assessment Plan (ORAP); Army Operational Range Assessment Program (ORAP); Marine Corps Range Environmental Vulnerability Assessment (REVA); and Navy Range Sustainability Environmental Program Assessment (RSEPA).

1.2 Meeting Objectives

Over the past several years, SERDP, ESTCP, and the Army Environmental Quality Technology (EQT) Program have funded a significant body of basic and applied research to gain a better understanding of the MCs resulting from military training activities on ranges and to develop better sampling methodologies applicable for ranges, as well as technologies to treat or contain MCs in soil and groundwater. The results from these efforts are contained in numerous technical reports and papers but have not been integrated into standard or traditional environmental practice. In addition, there are no standards of practice universally accepted by the Services or the regulatory community for conducting range assessments or instituting potential management strategies.

The objectives of this technical exchange meeting were to (1) inform representatives from the range management and assessment communities of applicable technologies developed by SERDP, ESTCP, and the Army EQT Program and (2) identify technology needs of the range management and assessment community that could be addressed through additional research and development efforts supported by SERDP and ESTCP.

2 METHOD

The SERDP and ESTCP Technical Exchange Meeting on DoD Operational Range Assessment and Management Approaches was held 7–8 August 2007, in Annapolis, Maryland. Seventy-five experts participated, including DoD range managers, DoD range assessment program managers, contractors conducting or designing range assessments, and researchers (Appendix A: Attendee List). A steering committee composed of representatives from the various sectors assisted SERDP and ESTCP in defining the meeting's scope and determining its format.

Background papers were prepared and distributed prior to the meeting to communicate the state of the science in sampling and analysis methodologies and management strategies (Appendix B: Background Papers). The background papers and authors are listed below:

Energetic Munitions Constituents on DoD Training Ranges: Deposition, Accumulation, and Appropriate Characterization Technology, Dr. Thomas Jenkins, U.S. Army Corps of Engineers (USACE), Engineer Research and Development Center (ERDC)-Cold Regions Research and Engineering Laboratory (CRREL)

Near- and Long-Term Range Management Strategies: Sustainable Use of High Explosives on Operational Testing and Training Ranges, Dr. Steve Larson, USACE, ERDC-Environmental Laboratory (EL)

Two breakout sessions, each with three working groups, facilitated discussions of the current state of the science for range assessment and management and identified data gaps that could be addressed through additional research, development, testing, and evaluation (RDT&E) activities. In the first breakout session, participants reviewed current range assessment practices and identified any technical issues. The second breakout session focused on identifying technology needs that could be addressed through additional research and development efforts by SERDP and ESTCP in the areas of (1) characterization; (2) risk, modeling, and assessment; and (3) mitigation and management. The entire group participated in the final discussion and selection of the critical and high priority research and demonstration needs.

Research paths and demonstrations were prioritized as either critical or high priority, largely based on the sequence of events required to impact the assessment, mitigation, or management of operational ranges (Table 2-1).

Table 2-1. Definition of Research Need Prioritization

	Critical	High Priority
Research	Research that potentially could have a significant impact on the assessment, mitigation, and management of DoD operational ranges.	Research that is of high priority but may not be able to be initiated until critical research needs are addressed or may be more clearly defined after critical research needs are addressed.
Demonstration	Field demonstrations or assessments that can impact the near-term ability to implement improved technologies and strategies for the assessment, mitigation, and management of DoD operational ranges.	Field demonstrations or assessments that are of high priority but may not be able to be initiated until critical demonstrations or assessments are completed.

3 RDT&E NEEDS: CHARACTERIZATION

The Characterization working group was charged with identifying the state of the science and limitations and/or uncertainties associated with:

- A basic understanding of the characteristics (e.g., areal surface distribution) of the source terms created from ordnance items commonly used during live fire training exercises and the use of this information to guide the development of sampling strategies.
- Methods for sample collection, processing, and subsampling.
- Analytical methods for MCs (e.g., are methods available, are method detection limits adequate).
- Statistical approaches used for data analysis.

These topics served as a starting point for the discussion. The working group identified the needed improvements and the data gaps that could be addressed through additional research and development funding within each of these topic areas. In this vein, the working group also identified and prioritized research paths and demonstrations.

Relevant to characterization, the following sections provide a summary of the state of the science, limitations and uncertainties, and prioritized research and demonstration needs.

3.1 State of the Science

DoD has been concerned with residues of energetic compounds in the environment for well over 20 years. Characterization and subsequent remediation has occurred at many ammunition plants and depots, largely to eliminate sources of groundwater contamination from the production, storage, or destruction of either off-specification or out-of-date munitions, and the disposal of wastewater in lagoons. The major chemical compounds of concern have been those used as secondary explosives (2,4,6-trinitrotoluene [TNT]; 1,3,5-hexahydro-1,3,5-trinitrotriazine [RDX]; octahydro-1,3,5,7-tetranitro-1,3,5,7 tetrazocine [HMX]) and propellants (nitroglycerin [NG]; 2,4-dinitrotoluene [2,4-DNT]), the energetic compounds produced and used in the largest quantity. In more recent years, attention also has focused on perchlorate, an oxidizer used in solid rocket propellant. Only in the past ten years or so, however, has attention been directed at the presence and potential migration of MCs on military testing and training ranges.

3.1.1 Distribution

Based on extensive field research, the types of residues, their concentrations, and distributions differ depending on the type of range and munition used (Jenkins et al., 2006). For example, at hand grenade ranges, the major residue deposition occurs when grenades undergo a low-order (partial) detonation, either when thrown or when duds are blown in place using C4 demolition explosive. The major energetic residues on these ranges are RDX and TNT from Composition B, the explosive charge in M67 fragmentation grenades. For ranges where a recent partial detonation has occurred, concentrations in surface soils are generally in the low milligram per kilogram (mg/kg) range and the distributions are more spatially homogeneous than at other types of ranges where thousands of individual detonations continuously redistribute the residues.

At anti-tank rocket ranges, the major residue present in surface soils at the target area is HMX from the octol used as the high explosive in the warhead of 66-millimeter (mm) M72 light anti-tank weapon (LAW) rockets and the newer AT-4 rockets[11]. A concentration gradient is present in surface soils relative to the distance from targets (Jenkins et al., 2004). HMX concentrations in surface soils near targets are generally in the hundreds to low thousands of mg/kg with TNT concentrations about one-hundredth that of HMX. The high levels of HMX in the soil at anti-tank rocket ranges can be attributed to the high dud and rupture rate of the M72 rockets and the low solubility of HMX. Short-range spatial heterogeneity in residue concentrations at these sites is high.

At the firing points of anti-tank rocket ranges, NG is present from the double-base propellant used in the 66-mm M72 rockets. The major deposition of residue is behind the firing line due to the back blast from this weapon. Concentrations as high as a tenth of a percent have been found in soil up to 25 meters (m) behind the firing line (Jenkins et al., 2004). NG is also found between the firing line and the target, but concentrations are generally several orders of magnitude lower than behind the firing line.

Most of the acreage at artillery ranges (historical and currently used) remote from firing points and targets is uncontaminated with residues of energetic compounds. At artillery and mortar firing points, the energetic residues are associated with particles of nitrocellulose (NC) containing either 2,4-DNT or NG, depending on the type of propellant used for the specific firing platform, and residues can be deposited at distances up to 100 m ahead of the muzzle (Jenkins et al., 2007). For 105-mm howitzers, the major detectable residue is 2,4-DNT, which can accumulate to the mg/kg range for fixed firing points. The residues from the single-base propellant used with this weapon are distributed primarily as partially burned or unburned propellant (NC) fibers. Residue deposition and accumulation from 155-mm howitzers are much lower than that from 105-mm howitzers. Deposition from mortars is primarily NG from double-base propellants. Propellant residues are deposited at the soil surface and the highest concentrations remain at the surface unless the soil is disturbed. Propellant residues from mortars are greater than those from artillery.

Near targets at impact ranges the majority of munitions detonate high-order and deposit very little residue (Walsh, 2007). The major energetic residue deposition is due to low-order (partial) detonations, which can deposit chunks of pure explosive. Residue concentrations of hundreds or thousands of mg/kg are often found in the surface soils next to these low-order detonations (Jenkins et al., 2006). The primary residues are TNT and RDX from military-grade TNT and Composition B, the major explosives used in mortar and artillery rounds. The distribution of residues in the area of the range where detonations occur is best described as randomly distributed point sources. Some of these point sources may be due to low-order detonations from the blowing in place of surface unexploded ordnance (UXO) items. At present, the detection of these point source areas has been visual, but some initial research has been conducted to try to develop a near-real-time detection capability for these zones. The collection of representative samples in areas subject to these partial detonations is a major challenge.

[11] While the actual propellant used in the AT-4 rocket is proprietary, it is believed to be similar to that used in the M72 LAW rocket.

3.1.2 Soil Sampling

Site characterizations for environmental assessments have generally used what is commonly referred to as the grid-node sampling strategy. Using this strategy, the area of interest is divided into a number of individual grids (or exposure areas), the size of each being a function of the total area to be assessed. Within each grid, one (or perhaps several) discrete sample(s) is collected and shipped to an offsite laboratory where samples are processed and analyzed. The results of these analyses are assumed to be representative of concentrations within the grid and to be normally distributed because the numbers of samples are insufficient to assess the actual data distribution. The assumption that these discrete samples are "representative" of analyte concentrations within the grid is generally not tested, although the concentrations determined for replicate discrete samples collected from within the same grid often do not agree.

To test how diverse individual discrete samples might be from within firing points and impact areas, experiments were conducted at several different training ranges. In most cases, a 10-meter by 10-meter grid was established and was subdivided into 100 1-meter by 1-meter cells. A discrete sample was collected from within each cell and analyzed for energetic compounds according to established protocols (USEPA, 1994). The maximum to minimum concentration ratios varied from over two orders of magnitude to almost five orders of magnitude for these sets of 100 values, indicating that individual (or a mean of several) discrete samples could not provide reliable estimates of mean concentrations within grids as small as 10-meters by 10-meters. In fact, the maximum and minimum concentrations among nine discrete samples collected within a single 1-meter by 1-meter cell varied by two orders of magnitude, demonstrating the magnitude of very short-range heterogeneity in these areas. The median values for the 100 discrete samples within each data set were always less than the mean, and the standard deviations were always equal to or greater than the means, indicating that in no case were the concentration estimates from discrete samples normally distributed.

An alternate approach investigated was the use of multi-increment samples to estimate mean concentrations within grids (Jenkins et al., 2005). With multi-increment sampling, instead of collecting and analyzing single point samples, samples are built by combining a number of increments of soil from within the grid of interest to obtain a mass of sample of about 1 kg. These samples can be collected in a totally random fashion or more systematically. A series of sampling experiments were conducted at a variety of training range firing points and impact areas. Some of the areas sampled were identical to those where discrete samples were employed. The variability among replicate multi-increment samples was much lower than found for discrete samples within the same sample grids. For example, 2,4-DNT concentrations in discrete samples collected with a 10-meter by 10-meter firing point area at the Donnelly Training Area ranged over almost four orders of magnitude; whereas, concentrations among the ten replicate multi-increment samples from this area varied by only a factor of less than three, well within one order of magnitude. Similarly, the range in RDX concentrations for discrete samples from a 10-meter by 10-meter grid at a Fort Polk impact area varied by nearly five orders of magnitude; the range for multi-increment samples was reduced to less than two orders of magnitude. In addition, data from replicate multi-increment samples were found to be normally distributed in most cases; whereas, the data distribution of discrete samples was always non-normal. It is recommended that multi-increment samples be collected using a systematic random pattern rather than a totally random pattern that sometimes over- or under-represents various areas of the grid. In the systematic random pattern, a random starting point is selected and increments are gathered on an

even spacing as the sampler walks back and forth from one corner of the grid to the opposite corner.

3.1.3 Sample Processing and Analysis

Since the early 1990s, energetic compounds in soil samples have been analyzed using USEPA standard methods SW846 Method 8330 and Method 8095 (USEPA, 1999). The sample processing and analysis steps in these methods were developed to support the Installation Restoration Program, mainly for characterizing soils at ammunition plants and depots (Jenkins et al., 1989). The deposition of energetic residues at training range firing points and impact areas is quite different than that at ammunition plants where deposition was largely due to disposal of wastewater containing high concentrations of secondary explosives. Thus, the target analytes in Method 8330 were limited to the major secondary explosives, their manufacturing impurities, and environmental transformation products. The concerns about spatial heterogeneity in deposition were different than those for training range samples, and the disposition of the residues within the soil samples also is quite different.

Once samples arrive at commercial laboratories, common practice has been to remove a small portion of the sample for air drying. The remainder of the sample (often greater than 90%) is never processed. Any replicate analysis also comes from the same small portion that was removed and air dried. In training range samples, the analytes are largely present as particles of propellant or explosive and a large amount of heterogeneity exists within soil samples sent to the laboratory; concentrations in replicate subsamples can differ by a factor of ten or more. To minimize this source of uncertainty, the entire sample must be air dried and mechanically ground to reduce the particle size of the energetic residues present in the sample (Walsh et al., 2002).

Other changes that have been found to improve analyses for training range soils include: increasing the sieve size from 30-mesh (<0.595 mm) to 10-mesh (<2.0 mm) to include a portion of the particle size fraction that often contains energetic compounds; using 10 gram (g) subsamples and extraction with 20 milliliters of acetonitrile; allowing the use of extraction on a table shaker as well as in an ultrasonic bath; and including NG as a target analyte for the method (Walsh and Lambert, 2006). These changes have been incorporated in a new method, SW846 Method 8330B, which is recommended for training range soil analyses (USEPA, 2006). This method also includes a sampling appendix in which the recommended systematic random multi-increment sampling strategy is described.

3.1.4 Analytical Methods

General consensus was that currently available analytical methods identify major target analytes and have sufficiently low detection limits with the possible exception being nitroguanidine (NQ). For other analytes such as picric acid, agent breakdown products, tear gas, and NC, commercial laboratories have some capabilities but methodologies are not standardized. Some methods initially developed by the U.S. Army Toxic and Hazardous Materials Agency (now the U.S. Army Environmental Command [USACE]) are still in use for certain compounds. The lack of standardization has two potential concerns: comparability across the DoD Components and organizations and regulatory acceptance.

3.1.5 Statistical Methods for Data Analysis

Current practice within the environmental community is to rely on discrete samples to provide estimates of mean concentrations within exposure areas. Regulators, knowing that discrete samples often are not representative of exposure areas and wanting to err on the conservative side, have calculated 95% upper confidence limits (UCL) from their discrete sample database using a program called ProUCL. Experiments to test this approach using discrete samples collected within various exposure areas at ranges indicate that widely divergent estimates of the 95% UCL of the mean result from random selection of small numbers of discrete samples from larger data sets. However, when the same ProUCL approach is used with replicate multi-increment sample results, very consistent estimates of the 95% UCL of the mean are obtained for data sets as small as four.

3.2 Limitations and Uncertainties

The Services' current ORAPs estimate the source term largely by inference (e.g., understanding of inputs and perimeter sampling) due to the high costs, access issues, and safety hazards associated with access to impact areas. Lack of quantitative information regarding the source term limits the utility of predictive modeling regarding future adverse impacts and potential mitigation. This uncertainty, in turn, limits opportunities for implementation of best management practices (BMP) to contain MCs and prevent offsite migration. Further, accurate and targeted munitions expenditure tracking data are sparse. Although there is general acceptance that low-order detonations are the major source of residues, tools to monitor these events (current and legacy) are lacking. The operational nature of ranges dictates that tools for source identification and quantitation must be cost-effective to facilitate periodic reevaluations. In addition, tools are needed to facilitate integration of various data sources to provide weight-of-evidence information regarding sources. With detailed sampling, the inability to characterize sites in three dimensions is a current limitation for source estimation at open burn/open detonation (OB/OD) areas on explosive ordnance disposal (EOD) ranges.

Given a defined source of energetic residues, the question becomes how much will migrate and at what rate? An understanding of soil chemistry and hydrogeology is essential to predict fate and transport; however, site-specific environmental data associated with MC loading areas are rarely available. Further, more information is needed on dissolution from the source zone and partitioning between the solid and aqueous phases to more fully assess fate and transport issues.

With regard to sampling methods, soil sampling is minimal at present with both discrete samples and multi-increment samples being used. Increased outreach to the regulatory community is necessary to further support implementation of multi-increment sampling. With either approach, quality assurance/quality control (QA/QC) of the sample collection should be undertaken to ensure representativeness. Without such QA/QC, there is a high level of uncertainty in the results and associated management decisions. Although it is generally accepted that small numbers of groundwater wells are unlikely to provide adequate plume characterization, installing additional wells can be cost-prohibitive. Tools to optimize well placement—thereby maximizing the generation of useful data—are generally lacking. Lastly, while sampling methods do exist for characterizing water contaminants in situations such as dredging operations, these methods may need to be modified or validated for application at water ranges (freshwater and saltwater).

3.3 Research Needs

3.3.1 Critical Priority

3.3.1.1 Development of Characterization Approaches for Assessing Risk Posed by Munitions Constituents in Water Ranges

As compared to land-based testing and training ranges, significantly less is known about the fate and transport of MCs in water ranges (both saltwater and freshwater) in addition to a lack of applicable characterization protocols. The casings of underwater UXO and discarded military munitions eventually breach and release MCs through mechanical stress, corrosion, and low-order remedial detonations. These compounds can remain intact in the sediment, dissolve into the overlying waters, or bind to particles and be re-suspended into the overlying waters. Over time, various chemical, biological, and physical processes change the energetic compounds to other chemical forms having different transport and toxicity properties in various ecosystems. Although much work has been conducted on energetic compound transformation in terrestrial and groundwater systems, limited information is available on rates of attenuation or transport of energetics in coastal aquatic systems. Research is currently ongoing to improve the understanding of the fate and transport of MCs in fresh, brackish, and saltwater environments (SERDP ER-1431[12]). Based on fundamental information provided by this and other efforts, research is needed to develop characterization approaches and associated protocols for effectively assessing the risk posed by MCs in water ranges. These efforts should be informed by available data from photolysis studies on MCs and studies on the effectiveness of engineered and natural wetlands for MC treatment.

3.3.1.2 Source Zone Detection and Characterization Techniques

To support CSM development, an understanding of the source zone location and strength is essential. Because the largest source of explosives residues are areas where low-order detonations have occurred or where surface UXO have been ruptured by nearby detonations, it is these occurrences that must be located if mitigation activities are to be successful in reducing the mass of residues present on ranges and the potential for offsite migration. These occurrences may be highly dispersed on large artillery ranges or concentrated within a small area at small ranges such as demolition ranges or hand grenade ranges. In some cases, these areas can be visually located, but in areas with dense vegetation or areas that are inaccessible due to UXO, this will not be possible. Impact areas are often quite large, and it is not practical to try to identify areas where low-order detonations have taken place by large-scale soil sampling activities. Given their size, ongoing use, and inherent safety hazards, research is needed to develop remote sensing capabilities for rapidly screening operational ranges to identify the location of potential source zones (both legacy and current). For use at DoD munitions response sites, a suite of technologies has been developed and is now transitioning to field use for wide area assessment. Wide area assessments offer the opportunity to delineate target areas, eliminate uncontaminated land from the inventory, and collect quality data to enhance planning and risk assessment. These technologies are expected to significantly reduce costs, focus resources on risk reduction, and accelerate cleanup of munitions-contaminated land. Research is needed to assess the applicability of wide area assessments for characterizing MC sources. Remote

[12] http://www.serdp.org/Research/upload/CP-1431.pdf.

sensing, whether utilizing existing wide area assessment technologies or not, has the potential to significantly reduce costs associated with source identification and may also be used as a tool for confirming the effectiveness of range clearances.[13]

3.3.1.3 Sentinel Monitoring Techniques for Early Warning of Potential Receptor Impact Risk

Sustaining the future use of operational ranges requires an ongoing awareness of the mass and potential transport of MCs. While it is generally accepted that low-order detonations are the major source of residues, occurrences in the field are difficult to identify and hence are underreported. Research is needed to develop methods for real-time monitoring of low-order detonations. Accurate information on the extent of low-order detonations will improve efforts to detect and measure source terms. Soil and groundwater sampling and analysis are costly and often limited by ongoing range activities and conditions. There is a need for sentinel monitoring tools to identify and assess the potential for offsite contaminant migration without interfering with ongoing range activities or creating an undue risk to personnel. With regard to assessing and monitoring rates of transport, research is needed to develop and demonstrate cost-effective sentinel systems for in situ low-level detection and quantitation of MCs in soil or groundwater. Such sentinel systems may or may not be installed in monitoring wells. An ideal technology would allow low-level detection of target contaminants (e.g., RDX) and remote signaling to alert range management to potential receptor impact risks.

3.3.1.4 Development of Improved Fate and Transport Parameter Values for Munitions Constituents

Key factors in understanding the fate and transport of MCs are dissolution and partitioning between the solid and aqueous phases. Dissolution for explosives and release of propellant components from the polymeric NC matrix are the first steps in transport of energetic residues offsite, either vertically into groundwater aquifers or horizontally in surface runoff. Colloidal or particulate transport processes in overland flow also may be important. Ongoing research is addressing the rate of dissolution for various types of explosives (SERDP ER-1482[14]), and some initial experiments are under way to investigate the release of 2,4-DNT or NG from 105-mm, 5.56-mm, AT-4, and 81-mm illumination propellant. Additional studies are needed to address the rate of release of NG, 2,4-DNT, and NQ from propellant residues as a function of particle size. These data are critical to any realistic mathematical modeling of the fate of these components on ranges.

Studies show that MCs such as TNT, RDX, and HMX exhibit a relatively weak, yet positive affinity for solid phase partitioning in sediment/water systems. This partitioning is typically quantified in terms of a soil-water partition coefficient, or K_d, the most common metric used in transport codes. By design and for simplicity of use, K_d estimates "blend" the various chemical and physical retardation mechanisms that control sorption into a single parameter. Yet, applying solute K_d estimates from one soil/sediment system to another can result in order of magnitude

[13] Work group participants indicated that the USACE is currently working on the development of multi-spectral imaging of high explosive fragments on the training range surface. The technique involves digital imaging of training ranges and using sophisticated filtering and detection technology (that already exists). Challenges include signal processing, scale resolution, and effective deployment of detectors. (Personal communication with Dr. Mark Chappell, USACE ERDC)

[14] http://www.serdp.org/Research/upload/ER-1482.pdf.

errors between predicted values and observed results. One reason for this failure lies in the fact that soil/sediment systems contain heterogeneous distributions of charged, polar, and hydrophobic domains on the surface, that both interact with each other and with impinging organic solutes. MC sorption to the higher-affinity hydrophobic sites (generally represented by organic carbon contents) varies with the degree in which these domains are shielded by surface charge density, a parameter empirically determined by cation exchange capacity (CEC) measurements of the soils/sediments. Thus, poorly soluble MCs may partition differently to geological materials containing similar organic carbon contents but with different CEC values. Past attempts to improve K_d estimates by normalizing the coefficients against a specific property (e.g., organic carbon content) give a unitless estimate with limited utility in transport models. Furthermore, such normalizations assume linear changes in K_d, while, in fact, solid phase surface properties usually change nonlinearly for a variety of reasons, including shifts in the physical state of the solid phase itself. Errors in K_d-based predictions also arise from using inappropriate solid/solution (s/s) ratios in batch experiments. As a purely empirical parameter, the standard error in K_d estimates shifts dramatically with the magnitude of K_d itself and small differences in s/s ratios. Thus, research is needed to develop simple and inexpensive, yet standardized, protocols for generating robust K_d estimates that account for solid phase and statistical considerations.

In addition to an improved understanding of dissolution and partitioning between the solid and aqueous phases, research on the fate and transport of MCs in the vadose zone is needed. The vadose zone represents a conduit for contamination from the ground surface to the underlying water table. Vadose zone movement of MC should be affected by three processes: (1) interactions between the MC and the soil surface, (2) preferential flow paths burrowed out in soil by growing roots, and (3) interactions between the MC and the root surface. Currently, there is a lack of substantive experimental data to validate/verify the predicted transport of MCs due to these processes in the vadose zone. An improved understanding of fate and transport mechanisms in the unsaturated zone resulting in more accurate transport predictions is essential to assessing offsite migration potential. Specifically with regard to DNT, research is needed to elucidate the controlling transport mechanisms in the vadose zone (e.g., leaching of DNT from NC).

In general, heavy metals have been identified as a potential problem on ranges despite a lack of confirmatory experimental data. Research is needed to assess the vertical migration of heavy metals, particularly lead. Such an assessment will verify or refute the presumption to include this migration pathway in CSMs for small arms ranges.

3.3.2 High Priority

3.3.2.1 Assess Potential of Bag Burning Operations and Use of Spotting Charges to Generate Contaminant Source Zones

Bags of propellant powder are used with some artillery platforms at training ranges. The number of bags used depends on the distance to the target. At many ranges, bags of powder remain following training. While the use of burn pans is preferable, standard practice has been to line up these bags and burn them, which creates a hotspot of propellant residue. Research is needed to quantitatively assess the potential of bag burning operations to generate source zones of contamination. DNT, in particular, is of concern due to its concentrations within bags of

propellant powder. Although the USACE has investigated the potential for devices such as marking targets and spotting charges used by the Army to generate source zones, research is needed to assess the potential impacts of similar devices used by other military Services.

3.3.2.2 Improved Understanding of the Frequency of Unexploded Ordnance Rupture by Incoming Rounds

The rupture of UXO by nearby detonations represents a significant source of explosives residues; however, the frequency of UXO rupture in such situations is unknown. To improve source zone estimation techniques, research is needed to improve the general understanding and quantify the frequency of UXO rupture by incoming rounds. When combined with other sources of information such as low-order detonation rates, such data can assist efforts to define the potential strength of the source zone.

3.3.2.3 Improved Understanding of and Sampling Methods to Determine the Mechanisms Controlling Munition Constituent Concentrations in Surface Water

Concern over the potential for migration of MCs into surface water bodies is increasing. Migration into surface water bodies can occur from transport via overland runoff, subsurface transport (e.g., via seeps or groundwater), or from open water range training. Currently, there is a lack of data and information to rule out off-range migration of MCs via the surface water pathway as a major concern, especially when considering sensitive environmental receptors. There is a need to research the presence or absence of explosives in surface water systems and determine if any apparent (but unexpected) absence of explosives is due to some attenuation factors or perhaps to the fact that the actual mass of explosives present and available for surface water transport is very small. Further, there is a need to develop improved sampling methods for energetic compounds and metals in surface water. Using such methods, a time-weighted average of concentrations could be developed to provide representative concentrations.

3.3.2.4 Development of Analytical Methods for Future Munitions Constituents

MCs in use can change over time with efforts to develop more environmentally friendly versions and with evolving weapons systems, weapons platforms, and mission requirements. As an example, China Lake-20 (CL-20), a potential replacement for existing propellant and explosive materials, was developed by the Navy in the 1990s. The USACE ERDC-EL then developed analytical methods for CL-20 in environmental media. As new MCs arise, validated analytical methods must be developed and made available to enable reliable characterization of potential source zones and to assess migration to groundwater and surface water resources.

3.4 Demonstration Needs

3.4.1 Critical Priority

3.4.1.1 Improved Methods for Developing Conceptual Site Models and Applying Data Quality Objectives for Water Ranges

Building on the research needs previously identified for water ranges, including fate and transport as well as characterization protocols (see Sections 3.3.1.1 and 3.3.2.3), improved methods for developing CSMs and applying DQOs need to be developed and demonstrated.

Sources, pathways, and receptors as well as transport mechanisms differ in aquatic environments; specific approaches relevant to these environments are needed.

3.4.1.2 Development of Decision Guidelines for Optimizing Groundwater Well Placement on Operational Ranges

Although it is generally accepted that small numbers of groundwater wells are unlikely to provide adequate plume characterization, installing large numbers of wells can be cost-prohibitive. Tools to optimize well placement are generally lacking. There is a need to develop and demonstrate decision guidelines for optimizing well placement in applications relevant to operational ranges. Sites such as the Massachusetts Military Reservation (MMR) underwent numerous iterations of costly well installations before locating the contamination. There is a need to assess lessons learned from MMR and other operational ranges with regard to groundwater well placement. Such assessments may glean useful information to augment decision guidelines.

3.4.2 High Priority

3.4.2.1 Improved Source Zone Estimation Techniques Not Dependant upon Site Sampling

Extensive sampling to locate and quantify source zones is not always warranted or possible given limited resources and safety concerns. Techniques to improve source zone mass estimation and the associated modeling to predict offsite migration of MCs are needed. Specifically, there is a need to demonstrate and validate existing source estimation techniques that do not involve sampling. Without such an assessment, there is a high level of uncertainty associated with the utility of results predicated on such estimates. There is also a need to look at those installations known to have off-range contamination and identify what specific environmental factors are causing that contamination so that future investigative efforts can be more efficiently applied. Compilation of data from operational ranges with known off-range contamination as well as formerly used defense sites investigated through the Military Munitions Response Program (MMRP) has the potential to assist source identification at other ranges.

3.4.2.2 Integration of Multi-Increment Sampling into the Triad Approach

The Triad approach (ITRC, 2005b) to decision making offers a technically defensible methodology for managing decision uncertainty that leverages innovative characterization tools and strategies. The Triad refers to three primary components—systematic planning, dynamic work strategies, and real-time measurement systems. Specific to operational range settings, there is a need to integrate multi-increment sampling in the Triad approach. On ranges, MCs are heterogeneously distributed across even short distances. With multi-increment sampling, instead of collecting and analyzing single point samples, samples are built by combining a number of increments of soil from within the grid of interest using a systematic random pattern (Jenkins et al., 2005). Multi-increment sampling yields results that are more representative of field conditions, thereby reducing uncertainties and improving the accuracy of assessments of the potential for offsite migration.

3.4.2.3 Development of Early Warning Mechanisms to Inform Sustainable Range Management Decisions

Sustaining the future use of operational ranges requires an ongoing awareness of the mass and potential transport of MCs, an awareness that depends in large part on the availability, accessibility, and accuracy of content in a database. In support of sentinel monitoring systems (e.g., early warning systems) for operational ranges, there is a need to develop a consistent database to track expenditures, locations/targets, low-order detonations, and dud rates as well as tools to automatically gather data. These types of data are currently available and utilized to an extent; however, there is a high level of uncertainty with regard to completeness and accuracy. The establishment of a more accurate estimate of low-order detonation rates for each of the major munitions types could, when combined with expenditure date, be used to estimate source loading. Mechanisms for communicating important information—such as numbers and locations of duds and low-order detonations between operators and managers, between operators and trainers, and between operators and developers/testers—are not well-established. In addition to the data collection/tracking needs, research is needed to develop a cost-effective sentinel monitoring method for RDX in groundwater that could be widely deployed to provide data to inform range management decisions. Cost-effective field analytical methods are currently available for RDX in groundwater (e.g., immunoassay field method), but a cost-effective early warning tool or method to alert range managers to the presence of RDX in groundwater beneath their range impact areas is needed.

3.4.2.4 Development of Munition Constituent Performance Standards for Quality Assurance/Quality Control at Analytical Laboratories

In the past, MC performance evaluation standards for QA/QC were required for laboratories conducting analyses. Work group participants recommended returning to this approach as a means of improving the representativeness of samples and utility of results. Efforts are needed to develop and implement MC performance evaluation standards for QA/QC at analytical laboratories based on the state of the science in sample handling and processing.

3.5 Needs Mentioned but Already Being Addressed

The Characterization working group noted two RDT&E needs (identified below) that are already being addressed to a large extent through various organizations. The interest of participants in these topics elevates the importance of effectively transitioning results to support rapid implementation in the ORAPs.

3.5.1 Characterization of Source Zones for Nitroguanidine

NQ is used in triple-base propellants at ranges when the distance to target is greatest. Characterization of source zones for NQ is a planned component of SERDP project ER-1481[15] being conducted by the USACE ERDC-CRREL. To date, researchers have had difficulty locating a range within the United States with NQ. Collaboration with Canadian researchers has identified the Canadian Forces Base Suffield in Alberta, Canada, as a potential sampling location

[15] http://www.serdp.org/Research/upload/ER-1481.pdf.

for triple-base propellant firing points. British Army live-fire training exercises using 155-mm artillery British guns and 120-mm United Kingdom challenger tanks (both systems using triple-base propellants) will be conducted at Base Suffield in May or June 2008. Discussions are under way to coordinate sampling during these training exercises.

3.5.2 Distribution and Fate of Propellant Residues at Small Arms Ranges

Under SERDP project ER-1481[16], researchers from the USACE ERDC-CRREL are defining the distribution and fate of propellant residues associated with firing munitions. A technical report on the accumulation of propellant residues at small arms ranges as well as characterization guidelines is slated for publication in early 2008.

[16] http://www.serdp.org/Research/upload/ER-1481.pdf.

4 RDT&E NEEDS: RISK, MODELING, AND ASSESSMENT

The Risk, Modeling, and Assessment working group was charged with identifying the state of the science and limitations and/or uncertainties associated with:

- The understanding of the physicochemical parameters and the degradative half-lives of MCs for use in predictive fate and transport modeling.
- The adequacy of quantification of risk to various types of receptors.
- The adequacy of existing toxicity data to determine the risk from MCs.
- The adequacy of existing exposure methods/models to determine the risk from MCs, especially where access to sites is limited/controlled.

These topics served as a starting point for the discussion. The discussion was not, however, limited to these topics, and in some instances, the initial topics were modified to address issues the group believed were more relevant. The group identified the limitations and uncertainties in the current state of the science and identified data gaps that could be addressed through additional research and development funding.

The following sections provide a summary of the key issues identified by this working group and a prioritized list of research and technology demonstration/validation efforts required to address the data gaps.

4.1 State of the Science

To assist in defining the state of the science and identifying the existing data gaps, the group used the Risk Assessment paradigm developed by the National Academies of Science (NAS) (Figure 4-1). This paradigm provided a means to structure the group discussion. Thus, the state of the science and limitations and/or uncertainties were identified in four areas: Hazard Identification, Toxicity Assessment, Exposure Assessment, and Risk Characterization.

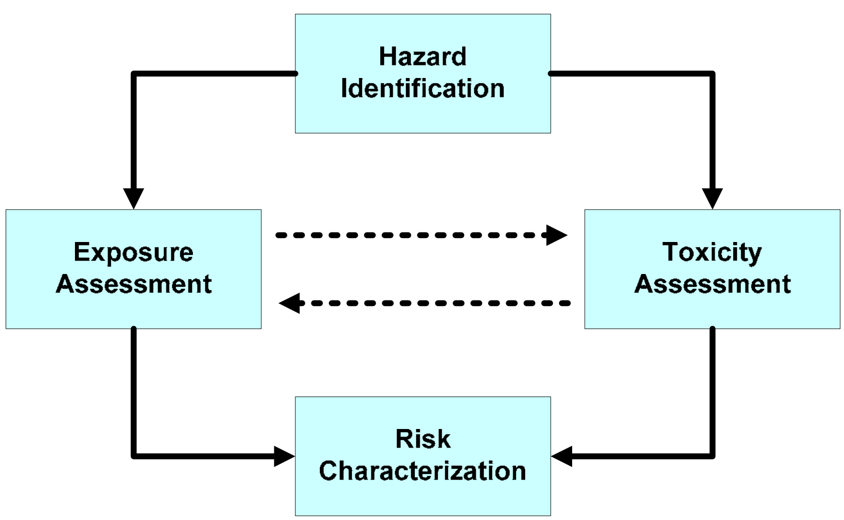

Figure 4-1. Risk Assessment Framework (NRC, 1983)

Risk Assessment in the Federal Government: Managing the Process (NRC, 1983) presented a conceptual framework for risk assessment. Risk assessment is defined as "the characterization of the potential adverse health effects of human exposures to environmental hazards." The overall scheme and terminology proposed in the 1983 report entailed hazard identification, dose-response assessment (now termed 'toxicity assessment'), exposure assessment, and risk characterization. The specific parts of the risk assessment process are defined as follows:

- Hazard identification is defined as "the process of determining whether exposure to an agent can cause an increase in the incidence of a health condition," including "characterizing the nature and strength of the evidence of causation."
- Dose-response/toxicity assessment is defined as "the process of characterizing the relation between the dose of an agent administered or received and the incidence of an adverse health effect … as a function of human exposure to the agent," accounting for exposure intensity, age, sex, lifestyle, and other variables affecting responses to hazardous agents.
- Exposure assessment is defined as "the process of measuring or estimating the intensity, frequency, and duration of human exposures to an agent currently present in the environment or of estimating hypothetical exposures that might arise from the release of new chemicals into the environment."
- Risk characterization is defined as "the process of estimating the incidence of a health effect under the various conditions of human exposure described in exposure assessment. It is performed by combining the exposure and dose-response assessments. The summary of effects of the uncertainties in the preceding steps is described in this step."

The state of the science and the limitations and/or uncertainties associated with each of the four parts of the risk assessment process, as applied to operational ranges, is discussed in the following sections.

4.1.1 Part 1: Hazard Identification

Hazard identification is the first non-quantitative step in a risk assessment. The objective of hazard identification in a risk assessment is to determine whether the available scientific data describe a causal relationship between an environmental agent, in this case a MC or other range-related chemical, and a demonstrated injury to human health or the environment. In humans, the observed injury may include such effects as birth defects, neurologic effects, or cancer. Ecological injuries may include fish kills, habitat destruction, or other adverse effects on the natural environment. Information on the chemicals responsible for the effects may come from literature reviews, models, or laboratory studies in which test animals were deliberately exposed to chemicals. Direct measurements of chemicals in environmental media are also important. In most cases, the primary issue is whether a causal link can be established between the chemical and the injury. In some cases, however, identification of the specific chemical thought to be causing the harm may be an issue if the chemical's identify is not known based on chemical release records or analytical testing.

The main issue identified by the working group was that many of DoD's current data systems are not useful for hazard identification. Data on chemical releases on ranges are either collected but not used or the data are not collected at all. There is a need to transform the available information (e.g., loading rate, exposure types, health effects, fate) into a format that makes the data useful for hazard identification and decision making for range sustainability. Improvements in tools to gather and organize the abundance of data are required, although application of existing tools is currently lacking. In addition, data quality descriptors should be included with the available data so that users understand the limitations of the data. Second, there is a need to make more data on chemical releases on ranges available to risk assessors and modelers for use in all parts of the risk assessment process, but especially in the hazard identification step.

4.1.1.1 Identification of Range-Related Chemicals of Potential Concern

There are several MCs commonly associated with military munitions that are listed as environmental concerns or potential concerns (e.g., HMX, RDX, DNT, heavy metals). These MCs, as compared to the non-explosive MCs, are generally well-studied on a generic or macro level but poorly understood under most site-specific conditions. An extensive study by Pennington et al. (2001, 2002, 2003, 2004, 2005, and 2006) and Clausen et al. (2004, 2006) at Camp Edwards, Massachusetts, identified a list of MCs that were considered important to monitor. While MCs are the primary chemicals typically associated with ranges because of their use in munitions, chemicals other than those included on the 'standard' list of MCs also may exist on ranges (e.g., herbicides).

Current practice in hazard identification includes the use of archival searches, site personnel interviews, site visits, and the Army's Munitions Items Disposition Action System (MIDAS) database. While these activities often identify most of the chemicals used on the range, reliance on MIDAS may be problematic because the database does not contain all munitions used by the Services. Some Services have their own database systems available for identification of the potential MCs used in their munitions. The existence of a common munitions database is relevant for today's range managers, risk assessors, and modelers due to the increasing joint operations and training being conducted within the Services and would improve the understanding of what could potentially contribute to a source concentration (refer to Section 4.3.2.2). The working group was unable to identify a database of non-MC-related chemicals used on ranges (e.g., herbicides).

4.1.1.2 Identification and Description of Source Term

An accurate description of the source term(s) is critical to hazard identification. The Services' training requirements vary based on their specific requirements. For instance, one Service may require the use of munitions that another Service does not. Additionally, the use of the same ordnance item in different training scenarios by the Services is common; item usage rates and patterns affect the total amount of MC deposited at an impact area. In terms of source term modeling, various loading rates will change the hazard identification criteria. This is especially important because while the Services may use different ordnance items, they may use the same range facility as evidenced by the number of U.S. Air Force (USAF) ranges being assessed under another Service's ORAP.

Historical items such as the relic munitions discussed in Section 3 (e.g., the M72 LAW) that have been used on ranges or range complexes pose a potential challenge for source description

and modeling since the MCs associated with such items may not be contained in the MIDAS or other databases. In addition, ranges and range configurations will undergo changes to accommodate the dynamic training environments of the Services. Several configurations during the lifetime of the installation incorporating different munitions and munitions configurations complicate the understanding of environmental risks associated with the range.

In addition to historical munitions items, there also may be foreign munitions items on the range that would contain MCs of unknown origin. The extent of use and composition of foreign items may be known, but their effects on the environment may not be known due to a lack of record keeping when foreign munitions are used on the range.

Historical records or archives may be difficult to find or may be non-existent. Source descriptions may sometimes consist of previous range managers' memories of locations of firing and target points (Takasaki et al., 2006) or other locations where chemicals are released. Identifying the MCs possibly present in an impact area or chemicals released at other locations is subject to the record keeping by the installation range managers and users. The data collection requirements and quantification vary by Service in the way the expenditure data are collected, organized, and disseminated to range and installation offices. The actual number of munitions consumed or fired on the range is critical to source description. This information is kept in a log, but may not be conveyed to the installation managers that oversee the environmental aspect of the range operations and is thus not typically available to the risk assessment and modeling community.

Records of the actual amounts of material being deposited at a range are often known, but not transferred to range personnel. This may be caused by a disconnect between the range managers and the installation's environmental staff. Data systems that use a geographic information system (GIS) to identify and verify where munitions have landed in the impact area would be extremely helpful in source identification and description. Typically, this information is not collected in a manner suitable for analysis. This information could be used, along with other range management tools, for documentation of munitions impact, location, and detonation efficiency. These data could then be incorporated into risk, modeling, and assessment efforts by range managers and installation staff.

Although MIDAS and other available databases provide the percent composition of the MCs that comprise the munitions, there is some concern as to what is actually being deposited on the impact area. Access to the impact area is often difficult to obtain for various reasons. "Bang box"-type studies are often costly, but these studies are useful in identifying and quantifying the potential amount of MCs deposited on impact areas after detonation (although the potential exists for carry-over contamination between detonation tests). A series of real-world, low-order and high-order detonation studies have been conducted for a wide range of munitions (howitzers, mortars, hand grenades) with the collection of residues from snow-covered surfaces (Walsh, 2004; Hewitt et al., 2005; Jenkins et al., 2002; Pennington et al., 2003). In addition, similar work has been done on the deposition of propellant residues at the firing points for mortars, howitzers, and small arms (Jenkins et al., 2006; 2007). A comprehensive assessment of available data from "bang box" and field studies as they relate to the MCs of concern contained in munitions listed in the MIDAS has not been performed. A better understanding of what is released and how it interacts with the environment would improve risk assessment and modeling efforts to estimate the environmental impact of range operations.

4.1.1.3 Additional Issues in Hazard Identification

Several data systems for hazard identification exist, but their usefulness is not being maximized. For example, release data from the Toxic Release Inventory (TRI) may be useful for determining the scope of the hazard presented on a range. However, the TRI database does not include a comprehensive list of explosives-related chemicals but does include metals above a given threshold. Other limitations of existing data systems include the inability to communicate with one another, provide comparisons between range complexes, or link to databases developed under other environmental programs. In addition, data collected by the Services as part of their range assessment efforts could be useful, but it was unclear if the data are being collected and stored in a manner that would facilitate hazard identification within and across the Services. For example, the ability of the USAF to provide data to the Army regarding the amounts and types of munitions dropped on ranges that belong to the Army is uncertain.

The current programs are focused on MCs associated with munitions items. An examination of other materials not related to munitions (e.g., pesticides, fuels) that may be used during training or testing activities on ranges is not included as part of the current ORAPs.

4.1.1.4 Consideration of Metals

Metals—in their pure state and contained in mixtures, composites, and alloys—are essential components of current munitions and include lead, copper, antimony, and tungsten. Metals are persistent in the environment, and some may bioaccumulate in biological systems. Metals are present on ranges as the result of training and testing activities as well as being part of the natural environment. This dual role as both pollutant (as a result of operations) and natural constituent presents a unique problem for those trying to assess the impacts of range use on human health and the environment. The duality of metals was recognized in the USEPA's 2007 guidance *The Metals Framework: Establishing a Process for the Consistent Application of Scientific Principles to Metals Risk Assessment*. The framework outlines key principles about metals and describes how they should be considered in conducting human health and ecological risk assessments. The principals outlined in the framework should be applied to range risk assessments.

4.1.2 Part 2: Toxicity Assessment

The toxicity assessment (i.e., dose response analysis) is designed to establish the quantitative relationship between exposure (or dose) and response in existing studies in which adverse health or environmental effects were observed. The toxicity assessment is based mainly on two extrapolations. The first extrapolation uses the relatively high exposure levels in most laboratory studies to estimate the probable magnitude of the effect in the same population at lower environmental levels where little or no data are available. The second extrapolation involves predicting the expected response in species (e.g., humans or ecologically important species) different from the laboratory animals studied.[17] As discussed later, each extrapolation involves numerous scientific uncertainties and assumptions, the impact of which must be explained in the risk characterization/uncertainty analysis.

[17] While the number produced in the toxicity assessment (e.g., a cancer risk value or a reference dose) is sometimes regarded as a risk assessment because it describes important information from animal and human studies, under the NAS paradigm and in most USEPA practice, a risk assessment is complete only when exposure assessment information is joined with dose-response analysis and all relevant information is used to characterize the risk.

Despite the work completed on ecological receptors, there remain large data gaps in the basic toxicity information available for large classes of ecological receptors. The working group completed a rudimentary data gap identification process and noted data gaps for NG and DNT (various isomers) with regard to bird and amphibian species.

In some instances, the toxicity data available for use in conducting risk assessments, modeling efforts, and environmental assessments of MCs may not be adequate or may be based on invalid information. For instance, some information may be based on studies that do not have relevance to the area that is of interest. The question for the risk assessors and modelers is to decide the relevance of the toxicity data and to attempt to either validate the data with additional studies or to use the data as it exists. The benefit of additional RDT&E efforts focused on validating existing data may not be worth the cost and effort involved, while more knowledge may be gained by filling the data gaps with missing information. A concerted effort to focus on current and emerging contaminants and their toxicity effects would be more beneficial; incorporating such studies prior to the use of new munitions may decrease the reactionary effect commonly encountered after new munitions are used.

The use of data that does not reflect site-specific conditions, essentially where the information obtained in a laboratory setting does not or would not be relevant in the environment that is of interest, is also a concern. For instance, toxicity data based on high laboratory dosage levels that may not or would not be observed under the range conditions can lead to invalid risk assessment and modeling results. The ability of a receptor to ingest the MCs on a regular basis as was conducted in the laboratory, not taking into account other interactions such as the degradation of the MCs, can also make the toxicity data questionable. The exposure of a test organism to single MCs does not accurately reflect field conditions where organisms are exposed to multiple chemicals.

The general state of knowledge regarding the toxicological, chemical, and physical properties of MC by-products is lacking. Data gaps exist in understanding the mobility, toxicity, and bioavailability of the by-products relative to the parent compounds. While additional data on the effects of parent compounds is necessary, there needs to be a compromise between conducting research on MCs where some data exists versus getting valid data on MC by-products (and emerging MCs) where no (or very little) data exists.

Although SERDP and ESTCP do not typically fund human health-related toxicity projects, the working group noted that data gaps exist in both chronic and acute human health toxicity data for select MCs and their by-products. The USEPA often uses uncertainty factors to account for incomplete or missing data when developing toxicity benchmarks. The factors are intended to account for (1) variation in susceptibility among the members of the human population (i.e., interindividual or intraspecies variability), (2) uncertainty in extrapolating animal data to humans (i.e., interspecies uncertainty), (3) uncertainty in extrapolating from data obtained in a study with less-than-lifetime exposure (i.e., extrapolating from subchronic to chronic exposure), (4) uncertainty in extrapolating from a lowest observed adverse effect level (LOAEL) rather than from a no observed adverse effect level (NOAEL), and (5) uncertainty associated with extrapolation when the database is incomplete. The sum of all uncertainty factors for a given chemical often exceeds 1,000; e.g., the total uncertainty factor for naphthalene is 3,000. However, the USEPA is open to removal or amendment of the factors if additional toxicology data becomes available. Thus, the development of complete human health toxicity data sets for the MCs of concern is critical.

4.1.3 Part 3: Exposure Assessment

The exposure assessment moves the risk assessment from the study of known receptors in which dose (exposure) and response are measured together to the task of identifying and characterizing exposure in other potentially exposed populations (i.e., those outside of the laboratory). These receptors may be groups as broad as the population of a nation for certain widely distributed materials (e.g., contaminated food) or limited to certain occupations or user groups (e.g., range workers). Questions raised in the exposure analysis concern the likely sources of the pollutant (e.g., target areas, firing points, leaking duds, pesticide application), its concentration at the source, its pathways (air, water, food) from the source to target populations, and actual intakes (doses) impacting receptors.

The main exposure assessment tools used by the risk assessment and modeling communities rely on measurements of the type and quantity of a pollutant in various environmental media and, when available, in plant or animal tissues, and are used to project expected exposure levels in individuals, populations, or both. The exposure analysis also develops "lifestyle" data to identify and describe populations likely to contact a pollutant. For example, if a MC that causes developmental effects in test animals is bioaccumulated in fish, the exposure analysis would consider "lifestyle" information such as the number of people who eat fish from areas impacted by the range, how often fish was consumed, and in what quantities. To complete the exposure analysis, the lifestyle information is combined with information on how much chemical (most likely measured at very low levels) remains in fish when sold or caught for consumption.

4.1.3.1 Fate and Transport

The movement of MCs and other range-related chemicals through the environment as determined by mathematical models is the main exposure assessment tool used by the risk, assessment, and modeling community. Understanding the MCs and how they interact with the environment is critical to the risk, assessment, and modeling effort. Challenges associated with accessing impact areas inhibits the ability to understand what happens in the impact area, what is in the impact area, and what source concentrations are feeding the fate and transport of the MCs.

The gaps in current understanding of fate and transport properties of MCs range from site-specific uncertainties to general unknowns depending on the specific chemical. Currently, values of undefined parameters are either assumed or presumed to be similar to a known compound and then used in fate and transport models. Fate and transport modeling parameters include particulate versus soluble form, colloids and sediment transport, physical transport issues, dissolution rates, octanol-water partition coefficient (K_{ow}) and K_d, and degradation rates and by-product formation. Examples of these parameters are discussed below:

- Particulate versus Soluble Form: The MCs' ability to move in the environment in either the particulate or soluble form, and the equilibrium interactions of the MC and how it will interact with the surrounding and changing environment
- Colloids and Sediment Transport: The interaction of MCs with colloids and sediments, and the ability of the colloids and sediments to transport or potentially transport the MC
- Physical Transport Issues: The physical characteristics of the MC in the environment that inhibit or enhance the transport of the MC

- Dissolution Rates: Laboratory dissolution rates of many MCs are known. A change in environment and soil type may drastically change the dissolution rates, specifically, the dissolution rates of metals.
- K_{ow} and K_d: The octanol:water ratio is a relatively common and known parameter for most organic MCs and can be converted to a sorption factor, K_d. The K_d for metals in different soils can also be determined, but for metals there is not an easy conversion from K_{ow}.
- Degradation Rates and By-Product Formation: Laboratory degradation and by-product formation rates can be easily calculated under various conditions and then used in models.

Three important basic parameters used for fate and transport models—vapor pressure, Henry's Law constants, and solubility—are important in exposure modeling and risk assessment and, as a group, are well-known and understood for RDX, 2,4-DNT, 2,6-DNT, and HMX (Dortch et al., 2005). Data is lacking on these parameters for NG and the amines of DNT.

4.1.3.2 Source Concentration

The source concentration is often difficult to determine due to several factors such as access to the impact area, knowing the number of high-order versus low-order detonations, and understanding the amount of MCs that remain after either a high-order or low-order detonation. The source term is best estimated based on known expenditures fired at each target; however, these data are often lacking. Several issues regarding exposure assessment parameters need to be addressed: dissolution rates, onsite concentrations leading to offsite exposure, spatial distribution of the MC (source distribution and mass), area of concern (AOC)/source area, distance to receptor (two-dimensional [2-D] models), pathway to receptor (food chain transfer), and neat compounds vs. field compounds.

- Dissolution Rates: As stated above, with respect to fate and transport models the dissolution rate of the source concentration is often difficult to determine due to the dispersible and heterogeneous nature of MCs in the source term.
- Onsite Concentration Leading to Offsite Exposures: Understanding how the source concentration is related to the concentration present in an offsite exposure area is important in determining the exposure assessment.
- Spatial Distribution of the MC (mass onsite is unknown): Since source areas typically have restricted or limited access, determining the onsite concentration of the MC may be difficult, but may be estimated using source estimation tools such as expenditure tracking.
- AOC/Source Area: Even when the source area concentration is known or estimated, it may not coincide with the AOC. The exposure area may be far from the source area; understanding how the source area MC concentrations are associated with the AOC of interest is important in determining the exposure assessment.
- Distance to Receptor (2-D Models): Typically, a 2-D model is required to estimate the fate and transport of an MC from the source zone to the receptor, taking into account the vertical and horizontal transport of the MC from the source zone.

- Type of Pathway (Food Chain Transfer): There are several pathways through which a receptor can be exposed to the MC. One of the most common is through food chain transfer. Understanding the transformation and movement of MCs through the food chain and the effects that the MC has on the receptor can provide support for the exposure assessment (food chain transfer should also examine degradation by-products potentially produced in the food chain).
- Neat Compounds vs. Field Compounds in the Source Area: Typically, benchmark tests are conducted with neat or laboratory grade MCs. These neat compounds are typically tested without additional compounds present. An understanding of the interactions between different MCs (when present as co-contaminants) is critical in determining the interactions and effects that occur at the source area and their exposure potential to receptors.

4.1.4 Part 4: Risk Characterization/Uncertainty Analysis

Although each of the preceding parts of the risk assessment paradigm examine all relevant data and information to describe hazard or dose-response or exposure, under the 1983 paradigm conclusions about the overall risk cannot be reached. The overall risk conclusion (and the certainty in the estimate) is reserved for the final analysis where information, data, and conclusions from each of the preceding parts are examined together to fully describe the expected risk by comparing the exposure predictions for real-world conditions to the available dose-response information from animals, people, and special test systems.

4.1.4.1 Risk Characterization Integration Tools and Efforts

Risk, modeling, and assessment efforts will not be effective if the range managers and installation staff do not (1) have the tools to effectively integrate the available data, (2) take the appropriate actions to conduct the risk, modeling, and assessment activities, and (3) implement risk reduction strategies.

The risk assessor and modeler can integrate the munitions training and range use records into their efforts to predict MC concentrations in the soil and relate these to potential groundwater and surface water concentrations. There are existing models (e.g., Adaptive Risk Assessment Modeling System [ARAMS™]), but a more quantitative model could potentially be developed and validated with the data that can be generated through RDT&E efforts as well as data collected from training events on active ranges. Risk assessors and modelers can incorporate visual and GIS data generated by the range users and managers to determine the source zone MC mass. By determining such parameters as the degradation rate and by-product production, predictive models and risk assessments of range use could be incorporated into the range management strategy, potentially increasing the ecological life-span of the training areas. Food chain models used to understand and predict the bioaccumulation and biotransfer of MCs and their potential degradation by-products could also be provided by modelers and risk assessors.

There may be a communication gap between range managers and installation environmental staff because the two have separate missions to perform. The range manager’s focus is to train personnel while the installation environmental staff’s mission is to protect the environment. While the two missions are very important, it is critical that the range managers appreciate the importance of environmental protection and understand the requirements for the environmental mission to be accomplished. Communication and education of the needs and importance of risk

assessment for range managers can be a tool to facilitate and integrate better communication between the two groups. The Army's Integrated Training Area Management (ITAM) program currently focuses on soil erosion issues, but could be modified to be used as a guide by all Services to administer environmental stewardship while meeting the necessary training requirements. Aspects of ITAM that should be carried forward include carrying capacity models for munitions, use capacity incorporation, and maximum throughput on ranges. The user-friendliness of the risk assessment and modeling tools could be improved by providing:

- Results in a qualitative manner (i.e., "poor," "good," or "best"),
- Comparisons optimized from multiple sets of basic options,
- Default values for many standard training scenarios to maximize model usability,
- Options for quantitative answers suitable for in-depth analysis of range management strategies,
- Information to installation staff by range managers such as expenditure tracking, operational tempo, and visual and GIS assessment of munitions impacts and detonations, and
- Outputs that support the development of BMPs on ranges.

4.1.4.2 Uncertainty Analysis

There is a large amount of uncertainty and variability associated with the current risk assessment and modeling tools available for assessing ranges. The uncertainty exists due to an inability to accurately reflect natural conditions and processes. The variability is a result of the naturally occurring array of potential conditions possible. The tools for addressing and communicating variability and uncertainty are not well developed. Even the upper and lower bounds of the possible or plausible answers are not well known. Due to the physical hazard associated with conducting research in impact areas and in other areas where there may be UXO, some of the uncertainty and variability may never be completely characterized.

4.2 Research Needs

4.2.1 Critical Priority

4.2.1.1 Improved Understanding of the Role of Valence State in the Fate, Transport, and Toxicity of Heavy Metals Associated with Munitions Constituents

Metals exist in the natural environment in different species with various valance states, which may change over time in response to variations in environmental conditions. In addition, the valence state of the metal when it is part of the munitions item or present as an MC may not be the same as that which exists naturally. The valence state of a metal affects its fate, transport, and toxicity and, therefore, its risk to potential human and ecological receptors. Soils can be highly contaminated with metals, but if the metal is present as a certain species, it may be nonbioavailable and thus represent an environmental non-hazard. In cases where metal speciation does represent an exposure risk, studies have been performed that demonstrate that the metal can be transformed into a stable species that is nonbioavailable (see Chappell and

Scheckel, 2007; Hettiarachchi et al., 2006; Hettiarachchi et al., 2003). A significant challenge in speciating metals is relating metals obtained by solution extraction of solid phases to the actual proportion of metal species on the surface. In recent years, new x-ray absorption spectroscopies (XAS) have been developed for the in-situ speciation of heavy metals adsorbed to soils.

There is a need to develop an improved understanding of the role that valence state plays in the fate, transport, and toxicity of heavy metals associated with MCs. Without such an examination, there will remain a high degree of uncertainty associated with the risk estimates for metals on ranges. The current risk models do not take into account the species or valance state of the metal. These models assume the metal is in a soluble form. Field validation of laboratory data regarding the effect of valence state on the fate, transport, and toxicity of heavy metals also will be needed to improve risk estimates.

4.2.1.2 Development of Analytical Methods for Munitions Constituents

Current regulatory-approved analytical methods do not permit testing of environmental media for all MCs that may be present on an operational range. For example, NQ is not currently a target analyte for Method 8330 or 8095. There is a need to develop and validate analytical methods for the range of MCs that may exist on an operational range. A critical element after the development and validation of new analytical methods is the acceptance and approval of these new methods by state and federal regulatory authorities. Efforts are therefore required to gain regulatory acceptance for new analytical methods that may be developed (see also Section 3.1.4).

4.2.1.3 Development of Toxicity Data for Munition Constituents and Munition Constituent By-Products

The general state of knowledge regarding the toxicological, chemical, and physical properties of MC by-products is lacking. Understanding the MCs' degradation by-products and the toxicity of the by-products is a data gap that should be filled. Data are needed regarding the mobility, toxicity, and bioavailability of the by-products relative to the parent MC compounds. While additional data on the effects of parent compounds is necessary, there needs to be a compromise between conducting research on MCs where some data exists versus getting valid data on MC by-products (and emerging MCs) where no (or very little) data exists.

There is a lack of information on some MCs and emerging MCs. For example, there are no carcinogenicity data available for the isomers of DNT (available data is based on mixed isomer formulations). The USEPA reports that 2,4-DNT "has not undergone a complete evaluation and determination under USEPA's Integrated Risk Information System (IRIS) program for evidence of human carcinogenic potential." The MCs lacking toxicity data may be of more concern than an MC for which there are some data (even though the current data may or may not be valid or up-to-date). An effort is needed to identify and rank data gaps for chemicals with no toxicity data. Only after the data gaps are ranked in terms of greatest possible risk should efforts be expended to perform basic research to develop toxicity data. The ranking of data gaps should be based on numerical or structural activity models to predict MC toxicity in the absence of any toxicity data.

4.2.1.4 Improved Understanding of the Fate and Transport Properties of Munitions Constituents as Military Grade Mixtures

The MCs present on operational ranges do not exist as neat compounds, though most laboratory studies are based on examinations of single compounds in a closed environmental system. The presence of multiple MCs may impact the fate and transport properties of the individual MCs. The presence of multiple MCs at an operational range is not adequately reflected in most laboratory-scale studies. There is a need to examine the fate and transport properties of MCs as military grade mixtures to better predict their fate and transport in the environment. Adequate data is lacking to understand the difference between the interactions of neat (or laboratory) grade MCs versus the military grade MCs that contain impurities such as plasticizers.

4.2.1.5 Development of Methodologies and Tools to Determine the Toxicity of Mixtures of Munition Constituents

As stated previously, MCs on operational ranges do not exist as neat compounds; they exist in mixtures with such things as impurities and plasticizers. The MCs at a range may interact with one another not only in the environment, where their fate and transport may be altered, but also after exposure occurs (e.g., inside the organism). Interactions of MCs inside the organism may affect the toxicity of the mixture. The interaction of MCs—either additive, antagonistic, or synergistic—makes prediction of the toxicity of mixtures difficult. Current practice, based on regulatory guidance, is to assume that the toxic effects are additive. Few examples of how to address the toxicity of mixtures exist and those that do exist are outdated.[18] The USEPA's official guidance on chemical mixtures is dated (USEPA, 1986). Therefore, there is a critical need to develop tools and methodologies to use in determining the toxicity of mixtures of MCs. Research on the toxicity of MC mixtures should focus on the relative percentages of the mixtures as they are found at the ranges.

4.2.2 High Priority

4.2.2.1 Development of Structured Process to Evaluate Quality of Existing Toxicity Data

For some range-related chemicals, there is a dearth of available toxicity data, while for others there is a relative abundance of toxicity data available in the open literature. However, the quality of the data varies with some studies performed to the highest standards of laboratory practice and others performed with no QA/QC provisions. There is a need for a structured, logical, and defendable process to evaluate existing data to determine which data are of sufficient quality for decision-making. Existing data should be judged not only on the laboratory performance criteria or statistical methods but also with regard to the relevance of the measured and reported outcomes for range issues.

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[18] The Agency for Toxic Substances Disease Registry is engaged in a multi-faceted course of investigation into the human health effects of chemical mixtures, including (1) identification of the mixtures of highest concern to public health, (2) estimation of the joint toxic action of these chemicals through assessment and laboratory methods, and (3) development of new methodologies for evaluating the health effects of mixtures (*see* http://www.atsdr.cdc.gov/mixtures.html).

4.2.2.2 Determination of Fate and Transport Parameters for Munitions Constituents in Varying Soil Types

The types of soil present at operational ranges may differ between firing point and impact point, from one impact point to another, and from one range to another. This heterogeneity of soil types at ranges results in uncertainties in estimates of the fate and transport of MCs in the environment whenever site-specific data is not available. A research effort is needed to increase the available data on the fate and transport parameters of MCs in multiple soil types corresponding with common soil types found at operational ranges. The additional data will improve fate and transport estimates and thus should improve risk estimates.

Three important basic parameters used in fate and transport modeling—vapor pressure, Henry's Law constants, and solubility—are important in exposure modeling and risk assessment and, as a group, are well-known and understood for RDX, 2,4-DNT, 2,6-DNT, and HMX (Dortch et al., 2005). Data is lacking on these parameters for NG and the amines of DNT. Thus, additional research is warranted to quantify the vapor pressure, Henry's Law constants, and solubility parameters for NG and the amines of DNT.

4.2.2.3 Development of Terrestrial Toxicity-Based (Chronic and Acute) Screening Benchmarks

Despite the work completed on ecological receptors, there remain large data gaps in the basic toxicity information available for large classes of ecological receptors. There is a need to support the further development of Eco-SSLs for MCs. The work group completed a rudimentary data gaps identification process and noted data gaps for NG and DNT (various isomers) with regard to bird and amphibian species.

The USEPA, with support from DoD, developed Eco-SSLs for several chemicals; however, the number of MCs for which soil screening levels are available is small (USEPA, 2003a). These screening levels represent concentrations of contaminants in soil that are protective of ecological receptors that commonly come into contact with soil or ingest biota that live in or on soil. These values can be used to identify those contaminants of potential concern in soils requiring further evaluation in a baseline ecological risk assessment. However, these values are only for chronic exposures, which may not represent all of the exposure conditions at an operational range.

There is a need for further development of subchronic and acute toxicity-based screening benchmarks for ecological receptors. Large data gaps exist when it comes to toxicity-based benchmarks for acute and subchronic exposure conditions. Given the sensitive life stages of some ecological receptors, subchronic data may be of critical importance when examining important endpoints such as reproduction. The additional benchmarks should be both dose-based concentrations (mg/kg/day) as well as media-based (mg/kg or mg/L) to facilitate their use in risk assessments and models.

4.2.2.4 Development of Aquatic Toxicity Data Sets for Munition Constituents to Support Development of Water Quality Criteria

Currently, there are several range-related chemicals of concern without state or federal water quality standards or guidelines relative to their toxicity to aquatic receptors. Water quality criteria for specific pollutants to protect aquatic life are developed in accordance with Section 304(a) of the Clean Water Act. The current criteria were developed in 1985 by the USEPA (Stephan et al., 1985) and are currently under revision (USEPA, 2003b). The updated criteria are

expected to be more data intensive than previous criteria. Changes are expected in the statistical methods used to derive the Final Acute Value (FAV) and the Final Chronic Value as well as the minimum database to arrive at a FAV for freshwater and saltwater receptors.

In order for ranges to monitor the impacts of chemical releases to aquatic receptors, there is a need to support the development of aquatic toxicity data sets for range-related chemicals (e.g., trinitrobenzene, dinitrobenzene, pentaerythritol tetranitrate [PETN], and other MCs [including metals; antimony, tungstate]). Additional effort should focus on statistical approaches for calculating the FAV from small data sets and determining a minimum database to arrive at a FAV. Research to compare static/flow-through and measured/non-measured tests with organic chemicals is needed. The development of rapid chronic tests as surrogates for life-cycle tests should be examined. Given the fact that many range-related chemicals are present on ranges for long periods of time, methods to predict chronic toxicity from acute and sub-chronic toxicity test data would be beneficial. In environments with limited water availability (i.e., ranges in the arid western United States), the effects of high concentration/short duration events should be examined. The effect of a high concentration pulse of chemicals in surface waters that may follow a rain event is not well characterized.

4.2.2.5 Development of Methodology to Select Representative Species as Indicators of Ecological Risk at Operational Ranges

The number and types of ecological receptors that may exist at a range can be very large (especially at the larger training and testing ranges) and may change seasonally or as on-range and adjacent land-use patterns change. Therefore, it is difficult to provide for environmental protection without selecting some specific organisms as representatives of the larger environment. While the problem of how to select specific ecological organisms as sentinel or indicator species was initially recognized in the USEPA's 1992 *Framework for Ecological Risk Assessment*, little work has been done in selecting organisms specifically to represent a range environment (USEPA, 1992; 1998). Therefore, additional research is required to define a means of selecting meaningful representative species to act as indicators of ecological risk at an operational range. Whether risk to these indicator species is measured in the field or modeled in the laboratory, the identification of such specific species must balance the unique constraints of data availability and ecological meaningfulness. In addition, the role played by socially significant (but biologically questionable) charismatic megafauna cannot be ignored.

4.2.2.6 Develop Improved Understanding of the Bioavailability of Munition-Related Heavy Metals in Terrestrial, Freshwater, and Marine Environments

Bioavailability is defined as the extent to which a substance can be absorbed and reaches systemic circulation. For environmental risk assessments involving soil and sediment, this definition implicitly includes the extent to which a substance can desorb, dissolve, or otherwise dissociate from the environmental medium in which it occurs to become available for absorption. The bioavailability of MCs will greatly affect degree of toxicity. The bioavailability of the MCs determined in the laboratory is not likely to be representative of the bioavailability of MCs observed in the field. Therefore, there is a disconnect between the toxicity of MCs tested in the laboratory and the actual toxicity of MCs in the field. DoD has made significant progress in advancing the state of knowledge regarding bioavailability (Battelle, 2003a; 2003b).

Despite recent advances in knowledge regarding the bioavailability of certain chemicals, specific knowledge about the bioavailability of most metals is limited. The MC with perhaps the largest current research program is lead. There is a need to expand the current state of knowledge regarding the bioavailability of MCs beyond lead and other select metals. While the need exists for data from freshwater and terrestrial environments, there is a need for expanded research into the bioavailability of metals in the marine environment. (See also related discussion in Section 5.1.1.)

4.2.2.7 Evaluation of Potential Release of Munition Constituents from Firing Points Located Near Installation Boundaries

The placement of firing points (relative to impact areas) can result in the firing point being located near the installation boundary, which may result in increased offsite releases of MC at firing points relative to impact areas. A review of range facilities where firing points are located near the installation boundary is needed, and research is needed to examine the types and amount of MCs released at these firing points. Information of this type has been and is being provided by ER-1481[19] for mortars, howitzers, and small arms. NG has been specifically addressed.

4.3 Demonstration Needs

4.3.1 Critical Priority

4.3.1.1 Development of Online Human Health and Ecological Toxicity Databases Including Data Quality Descriptors and Information on Benchmark Derivation

There are several online toxicity databases that modelers and risk assessment personnel can review and from which they can select toxicity data. Some of the existing tools contain links to the primary peer-reviewed literature (e.g., MedLine), but provide no information on benchmark derivation. Likewise, there are several online tools that contain toxicological benchmarks (e.g., the U.S. Department of Energy Office of Environmental Management Risk Assessment Information System) but contain no information on the quality of the primary literature on which the benchmarks are based. Existing online tools attempt to provide some coverage for both human and ecological toxicity data. However, there is a need for a single military-applicable online tool that provides links to the primary peer-reviewed literature, information on the derivation of benchmarks, and data quality descriptors for the primary literature and benchmarks. The data quality qualifiers are critical to the use of the system and its success in identifying usable data.

Many existing online systems attempt to be a one-stop location for toxicity data but do not include one or more necessary elements. For example, the USEPA's IRIS contains only data for human health toxicity but does not include ecological toxicity. Thus, the need for a comprehensive online tool for ecological toxicity is critical. The required system should be available to all users and have a transparent process for data review and exclusion/inclusion. The online system would have to be developed in cooperation with state and federal regulatory agencies so that its processes and procedures are acceptable for regulatory decision-making.

[19] http://www.serdp.org/Research/upload/ER-1481.pdf.

Once developed, the system would be useful for identification of data gaps or areas of weakness in the existing knowledge base.

4.3.1.2 Validate Existing Spatially Explicit Exposure Assessment Models Using a Variety of Receptor Types

The role of geographic diversity of species and their use of specific habitats for forage and other uses is not well integrated into most risk assessments. Most risk assessments—specifically ecological risk assessments—do not adequately consider the influence of habitat in determining the degree to which a receptor may be exposed. Current practice is to divide the receptors home range by the size of the AOC with no consideration of the habitat quality or habitat usage patterns. Given the size of many operational ranges and the size of many receptors' forage areas, the need for a better understanding of the spatially explicit nature of the exposure is critical. There is a need to validate existing exposure models that account for exposure in a spatially explicit manner. These models should be paired with ranges that have receptors with large and small geographic requirements for habitat usage. Validation efforts should examine multiple types of receptors (e.g., birds and mammals) that have vastly different habitat requirements.

4.3.1.3 Development of an Improved Understanding of Lead Bioavailability Based on Speciation

Perhaps one of the most well-studied of all range-related MCs is lead. However, the multiple forms of lead in the environment and the ability of lead to change form over time make this issue particularly vexing. There is a requirement for an improved understanding of lead bioavailability based on speciation using available protocols. Such projects should build on existing and previous SERDP and ESTCP projects that examined in vivo methods (SERDP ER-1166[20] and ESTCP ER-0517[21]). The demonstration project should focus on development of methods that allow risk assessment to move beyond default values for lead bioavailability. Lessons learned from lead may be able to support the development of a model or procedure for other range-related MCs (e.g., tungsten).

4.3.2 High Priority

4.3.2.1 Validation of Existing Dissolution Models for Metals

While the laboratory dissolution rates of many MCs are known, a change in environmental conditions and/or soil type may drastically change the dissolution rates. Specifically, the dissolution rates of metals under different environmental conditions may be affected. There is a requirement to validate existing dissolution models, especially for metals present in varying environmental conditions and soil types. Demonstrations should be completed in a wide range of soil types and in a wide range of environmental conditions. In cases where existing models do not adequately predict dissolution rates, new models should be developed.

[20] http://www.serdp.org/Research/upload/CU-1166.pdf.
[21] http://www.estcp.org/Technology/ER-0517-FS.cfm.

4.3.2.2 Compilation of Data on Munition Items Currently Not Included in the MIDAS

The currently available tools do not include data on the MCs in all munitions, especially historical munitions, torpedoes, foreign munitions, and some rocket systems. The most widely used tool—the Army's MIDAS—has significant limitations. Efforts to expand the system have progressed slowly. Therefore, there is a requirement to assemble and make available to researchers and decision makers data on munitions items not currently included in MIDAS. The ideal system would include data on MCs for items not in MIDAS as well as incorporate existing work by the Army on emissions factors.

4.3.2.3 Development of Guidance for Appropriate Application of Multi-Increment Sampling Methodology for Ranges

The USEPA provided guidance for composite or multi-increment sampling for the screening of soil hazardous waste sites in 1996.[22] The recent promulgation of USEPA SW846 Method 8330B for explosives sampling set a new threshold for the acceptability of multi-increment sampling. While useful for some applications, multi-increment sampling must be matched with the specific questions being examined. There is a requirement to demonstrate the instances where multi-increment sampling should be applied to support the risk, modeling, and assessment of ranges. Demonstrations of how best to implement multi-increment sampling strategies in support of range assessment, such as those recommended in Method 8330B, could be useful in assisting ranges in addressing complex issues with regard to exposure and source zone contributions.

4.3.2.4 Development and Demonstration of Forecasting Models to Predict Acceptable Munition Constituent Loading on Ranges

Demonstrations of models that can improve "forecastability" are needed to help ranges determine how much of a given MC can be applied or released at a range site without deleterious effects on human health or the environment. Forecasting tools like the Army's ITAM program are available to examine future land use conditions as a result of planned training and testing. The four major components of the ITAM program are Training Requirements Integration, Range and Training Land Assessment, Land Rehabilitation and Maintenance, and Sustainable Range Awareness. These components combine to provide the means to understand how the Army's training requirements impact land management practices, what the impact of training is on the land, how to mitigate and repair the impact, and communicate the ITAM message to soldiers and the public. Similar tools are needed to predict impacts from the release of range-related chemicals before they occur so that mitigation strategies can be developed and implemented prior to problems reaching a critical point.

4.3.2.5 Validation of Existing Fate, Transport, Exposure, and Toxicity Models to Include Identification of Advantages and/or Limitations

Significant research dollars have been invested on the development of multiple fate, transport, exposure, and toxicity models (e.g., SESOIL, MODFLOW, MT3D, SEAM). Some models (and sub-elements) are not fully validated with field data and published in the open peer-reviewed literature (see Dortch, 2001; Dortch and Fant, 2007; Dortch and Gerald, 2002; Dortch and

[22] *See* USEPA Soil Screening Guidance; Notice of Availability. 61 Fed. Reg. 27349. May 31, 1996.

Gerald, 2004; Dortch and Johnson, 2002; Gerald and Dortch, 2004; Gerald et al., 2004; Johnson et al., 2007; Sample et al., 2002; Lloyd et al., 2007a, 2007b). Additionally, limitations have been identified in the SESOIL model when used to model chemicals for which there is a distinct difference between adsorption and desorption phenomenon. There is a need to identify models requiring further validation, validate them, and provide discussion or comments on the advantages and/or limitations of the models in the peer-reviewed literature based on the fate, transport, and toxicity aspects of these models.

5 RDT&E NEEDS: MITIGATION AND MANAGEMENT

The Mitigation and Management working group was charged with identifying the state of the science and limitations and/or uncertainties associated with:

- Methods currently used by the range management community to prevent or limit the migration of MCs on ranges.
- Processes used to determine the application frequency of the range management methods.
- Processes used to determine the performance efficiency of the range management methods.

The operational constraints on the design and implementation of range mitigation and management strategies also were discussed. Regarding these issues, the group identified the improvements needed and the data gaps that could be addressed through additional research and development funding. Relevant to mitigation and management, the following sections provide a summary of the state of the science, limitations and uncertainties, and prioritized research and demonstration needs.

5.1 State of the Science

The readiness of the military forces depends on their ability to develop and test improved weapons systems and to train troops under realistic operational and wartime scenarios. Thus, sustainability of DoD's operational ranges is crucial to allow mission-critical testing and training activities to continue. Increasing concern that testing and training activities could contaminate ranges with residual MCs has threatened range sustainment. For example, in response to concerns that military training activities had contaminated the groundwater, the USEPA ordered the suspension of all live-fire training activities at MMR in 1997 (USEPA, 1997). Thus, the development and implementation of effective mitigation and management techniques to minimize the environmental impact of range activities is critical to the long-term sustainability of operational ranges.

The Mitigation and Management working group organized their discussion around four identified problem areas:

1. Small Arms Ranges
2. Impact Areas
3. Single-Site Explosive Ranges (e.g., EOD training ranges, OB/OD areas)
4. Streams, Sediments, Groundwater, Soils

Water ranges were also discussed by the Mitigation and Management working group. Issues raised regarding water ranges have been consolidated with those from the Characterization working group (see Sections 3.2, 3.3.1.1, and 3.4.1.1).

5.1.1 Small Arms Ranges

Small arms ranges are characterized by their small size relative to other types of DoD training ranges, the existence of established firing points, and the fact that the primary contaminants of concern (COC) to date have been heavy metals rather than energetic constituents. The principal environmental concern is the transport of metals into surface water bodies or groundwater and their potential to reach receptors at levels that exceed regulatory criteria. Although antimony, copper, lead, and zinc are released into the environment on small arms ranges, lead has been the primary COC based on its relative mobility, the concentration of the metal found in the soils on ranges, and the relative toxicity of the metal (Fabian and Watts, 2005). Implementation of management and mitigation methods is dependent on the potential for offsite migration of the metals (e.g., the presence of permeable and/or erodible soils and nearby surface water body). It was generally agreed that while horizontal transport of metals (overland transport via water flow into a water body) poses a potential concern at most sites, the concern regarding vertical transport of metals has not been adequately validated with experimental data (see Section 3.3.1.4).

Numerous methods have been developed to retard the transport of metals on small arms ranges and are described in BMP guidance documents (Fabian and Watts, 2005; ITRC, 2005a). These methods include:

- Operational changes to the use or maintenance of the range
  - Apply management guidelines to firing lane use
  - Minimize or eliminate firing into bodies of water or wetlands
  - Sustain vegetative cover on and around the range
  - Improve impact berm maintenance and repair practices
  - Implement inspection and maintenance programs for BMPs
- Structural enhancements
  - Improved berm design and construction techniques
  - Use of geosynthetic material as an impermeable barrier beneath the impact berm to contain mobilized metals in the unsaturated zone
- Storm water management
  - Flow diversion techniques
  - Runoff velocity reduction
  - Sediment trapping/containment
- Planting of vegetation on the range, berm, and in the buffer zone to minimize soil erosion and lead migration
- Soil amendments (e.g., lime, phosphate) to chemically stabilize soluble lead in soil pore water

- Bullet traps
- Periodic lead removal

Current sustainability methods for small arms ranges are well developed, although limitations and uncertainties exist due to site-specific factors. For instance, while the use of vegetation to control erosion and migration of metals is described in the BMPs, work group participants indicated that difficulties exist in identifying the optimum plants for specific geographic locations, range use scenarios, and soil lead concentrations. Similarly, although chemical stabilization methods (e.g., lime, phosphate) are proven to immobilize lead, uncertainties exist regarding the optimum application frequency and long-term reliability of this technology.

Regulatory criteria identifying the acceptable level of bioavailable lead are available for water, but there is a lack of regulatory criteria for the acceptable level of bioavailable lead in plants or soil. Development of additional guidance values would inform the application frequency of soil amendments and the selection of appropriate vegetation to control soil erosion and lead migration.

The vertical migration of metals continues to cause concern on small arms ranges despite a lack of experimental data. The development of an improved understanding of the vertical migration of metals, particularly lead, would inform the inclusion or omission of this pathway in a CSM (see Section 3.3.1.4).

Although active management practices such as the use of bullet traps to capture lead and vegetation have been developed to limit offsite MC migration, operational constraints on some small arms ranges can limit the applicability of these sustainment approaches. For instance, some small arms ranges are too large and extensive to allow the use of bullet traps. Furthermore, the use of vegetation to control erosion and lead migration can sometimes interfere with target viewing. In these situations, vegetation is eliminated through the use of herbicides. Likewise, demolition and hand grenade ranges have little or no vegetation.

Currently available small arms range sustainment approaches do not address the deposition and migration of energetic constituents deposited at the firing lines. There is increasing concern regarding the potential for NG, a component of the propellant contained in some small arms ammunition, deposition at firing lines. As an example, elevated concentrations of NG have been found near the firing line of the Tango Range at MMR. As a preventative measure, the excavation of soil impacted with NG has been proposed by the Massachusetts Army National Guard (MANG, 2007). Uncertainties associated with NG include its rate of environmental release from nitrocellulose, fate and transport, and the effects environmental NG contamination has on human health (see Section 3.3.1.4).[23] The development of an improved understanding of these issues would inform the need for management and mitigation methods to address NG contamination.

5.1.2 Impact Areas

Impact areas (where detonation occurs) are usually distinct and separate from the location where the weapon is fired. MCs found at impact areas are typically compounds used as high explosives

[23] Work group participants noted that the USACE ERDC-CRREL is planning to conduct preliminary batch and column adsorption/desorption studies for NG.

in the munition warheads or white phosphorus from smoke rounds (Pennington et al., 2006). Current practice to prevent or limit deposition and migration of MCs from range impact areas includes periodic clearance of the impact area and implementation of model target planning guidance.

Periodic range clearance of impact areas is performed to maintain range safety and sustainability. The extent to which the Services apply range clearance practices varies. Participants indicated that range clearance is routinely practiced by the USAF and Navy. The range clearance process may include the destruction of detected UXO; collection and replacement of unserviceable targets; and collection, sorting, and offsite transport of range scrap. Range scrap is composed of expended practice munitions, trash and debris, case fragments from live bombs, inert cannon projectiles, rockets, and expended target material (USAF, 2002). Likewise, Army and Marine Corps hand grenade and detonation ranges (OD, EOD, and combat engineer related) are routinely cleared after training, including EOD detonation or disposal of UXO. Larger artillery/tank ranges that utilize a central impact area are not commonly cleared. Some scrap may have value as a recyclable material due to its content of commercially viable metals. Before munitions items are recovered as scrap, they require demilitarization (removal of explosive residue and deformation of the item to render it unrecognizable as a military munition). Frequently, munitions items will be collected and consolidated in one area prior to being sorted. Because of the lack of thorough characterization of these materials, the potential for explosive residue to leach from items while stored prior to sorting is largely unknown or is not considered.

To minimize future human health and environmental impacts of range training activities, the Services have developed guidelines for the use, siting, and design of new ranges and target areas. The USAF has published guidelines for designing new targets primarily for use with the Bomb Dummy Unit (BDU)-33 munitions. The guidelines identify areas to examine for potential environmental impacts (e.g., threatened and endangered species, land, water, and air resources) that may result from the construction, operation, and maintenance of range sites on which the BDU-33 is used. These guidelines may also be incorporated into the reevaluation of BMPs for existing ranges and target areas, although the extent to which this occurs is unknown.

In addition to the current practices, several additional management and mitigation methods are in varying stages of research and development: surface soil amendments, phytoremediation, and the use of prescribed burns.

Soil amendment technologies have the potential to reduce the migration of MCs from surface soils to the underlying aquifer matrix and groundwater. The use of base hydrolysis technology to immobilize metals and degrade explosive constituents is being field-validated (ESTCP ER-0216[24]) at multiple grenade ranges. The technology is based on the premise that increased soil alkalinity caused by lime addition will decrease the water solubility of heavy metals and transform the explosive compounds in the soils. Results to date indicate a reduction in mass of RDX in soil pore water, sampled using field lysimeters, in areas where the surface soil was treated with lime (Larson, 2007; Davis et al., 2007; Larson et al., 2007). Field testing is anticipated to be completed in FY 2008. The use of biologically based amendment processes to enhance the immobilization and biodegradation of explosives residues is also under development (ESTCP ER-0434[25]). The amendment consists of peat moss—a low-cost, environmentally

[24] http://el.erdc.usace.army.mil/elpubs/pdf/trel07-5.pdf.
[25] http://www.estcp.org/Technology/ER-0434-FS.cfm.

friendly, long-lived, and high capacity sorbent—and soybean oil, a low-cost microbial stimulant. Laboratory validation has demonstrated the baseline effectiveness of the materials; field demonstrations validating that the amendments are easy to apply and effective are expected to be completed in FY 2009.

A significant amount of research is ongoing to advance the capabilities of phytoremediation for distributed source contamination on testing and training ranges. Laboratory and greenhouse studies using native and engineered plant systems are being conducted to increase the fundamental understanding of the uptake and transformation of explosive constituents in plant tissues or by microbial activity in the rhizosphere (SERDP ER-1498[26], ER-1499[27], ER-1500[28]). These efforts address TNT, RDX, and perchlorate contamination. Results are expected in the FY 2009–FY 2011 timeframe.

The use of fire ecology, the science of using fire to manage vegetation and ecosystems, has been investigated as an innovative approach to destroy explosives residues in surface soils (SERDP ER-1305[29]). Controlled or prescribed burning is used as a management technique in target areas for a variety of purposes: safety clearance prior to detection and demolition of UXO, wildfire avoidance, and plant and wildlife management. Controlled burns have the potential to destroy energetic compounds that are either associated with the vegetation that is burned or are in or on the surface soils heated by the fire. A field study was conducted at Eglin Air Force Base (AFB), Florida, to examine the impact of prescribed burning on the fate and transport of residual energetic compounds in surface soils on test and training ranges. The study demonstrated that prescribed burning can generate sufficient heat to destroy energetic residuals at ranges (DoD, 2006). Before this approach can be optimized and reliably applied in the field, an improved understanding of the underlying processes of thermolyses, sublimation, and melting/migration of the explosives residuals will be needed. Further development of the fire ecology technology should consider and incorporate existing data from thermal decomposition experiments conducted by explosives developers.

The primary challenges associated with applying management and mitigation methods for impact areas are the operational constraints imposed by ongoing range activities. These constraints include:

- Continuous range use (24 hours a day/7 days a week) for extended periods of time.
- Safety issues associated with personnel implementing a management or mitigation approach on active range impact areas (e.g., personnel involved with the application of surface soil amendments in impact areas).
- Mitigation methods that must be designed to withstand fire, explosive events, and range maintenance operations (e.g., regrading activities).
- Restrictions on habitat degradation.
- Unacceptable reductions in the performance standards (e.g., explosive power) of munitions.

[26] http://www.serdp.org/Research/upload/ER-1498.pdf.
[27] http://www.serdp.org/Research/upload/ER_FS_1499.pdf.
[28] http://www.serdp.org/Research/upload/ER_FS_1500.pdf.
[29] http://www.serdp.org/Research/upload/CP-1305.pdf.

5.1.3 Single-Site Explosive Ranges

Single-site explosive ranges (OB/OD areas and EOD training ranges) were considered separate and distinct from range impact areas due to their unique characteristics. OB/OD areas are typically permitted by the USEPA and are used to destroy unserviceable ordnance and their constituents. Disposal of munitions through OB/OD can generate kick-out and low-order detonations, dispersing explosive residue over wide areas. The practice of open burning of waste propellant bags was also discussed. EOD training ranges are used to train EOD specialists in the evaluation, safe rendering, recovery, and final disposition of ordnance.

Many of the mitigation and management approaches currently in practice or under development for small arms ranges and impact areas have the potential to be applicable at single-site explosive ranges (e.g., application of surface soil amendments, phytoremediation). It is unclear to what extent these approaches have transitioned or are under consideration for use at single-site explosive ranges.

A demonstration effort is ongoing to evaluate (1) the in situ degradation of energetic compounds within OB/OD soils as a result of natural plant-mediated degradation and (2) in situ enhanced aerobic and anaerobic bioremediation with low-cost additives to promote the degradation of energetic compounds within the shallow vadose zone pore water. The effectiveness of these two approaches for the reduction of RDX and HMX dissolved in vadose zone pore water in tropical soils beyond the root zone will be evaluated. The expected completion date for this demonstration is FY 2008 (ESTCP ER-0631[30]).

Development of sustainment approaches for single-site explosive ranges face many of the same operational challenges as do sustainment approaches for impact areas—safety issues, design requirements to withstand fire and explosive events, restrictions in habitat degradation, etc.

5.1.4 Streams, Sediments, Groundwater, and Soils

Treatment alternatives for energetic compounds in soils are fairly well-established, and they include soil washing, composting/landfarming, and anoxic biodegradation (Pennington et al., 1995; Boopathy and Manning, 1998; 2000; Widrig et al., 1997; Fuller et al., 2003). Additionally, a number of recently completed or ongoing efforts are focused on the further development of phytoremediation, surface soil amendments, and OB practices to remediate surface soil contamination (see Section 5.1.2). Unlike soils, however, efficient and cost-effective technologies for treating explosives-contaminated groundwater are very limited. Traditional methodologies for contaminated groundwater, which include pump and treat followed by granulated activated carbon filtration (Bricka and Sharp, 1993) and ultraviolet-oxidation (Bricka and Sharp, 1993), are either ineffective or very expensive for explosives treatment. In addition, bioremediation technologies that are applicable for remediating concentrated explosives (mg/kg–g/kg levels) in soils are generally not applicable for groundwater, where low contaminant concentrations (micrograms [μg]/L–mg/L) are likely to be present in large plumes.

Recent studies show the potential for both ex situ (Fuller et al., 2007) and in situ (Wani et al., 2002; Davis et al., 2004) treatment of nitramine explosives (e.g., HMX and RDX) in groundwater, and an ESTCP-funded field demonstration (ESTCP ER-0425[31]) is presently ongoing at Picatinny

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30 http://www.estcp.org/Technology/ER-0631-FS.cfm.
31 http://www.estcp.org/Technology/ER-0425-FS.cfm.

Arsenal, New Jersey, to validate in situ remediation. In the ESTCP-supported demonstration, cheese whey is being injected into an energetics-contaminated aquifer to promote biological reduction of TNT, RDX, HMX, and other energetic compounds. Final results of this project are expected in FY 2008.

Other technologies to treat energetic constituents in environmental media currently being demonstrated or recently validated include monitored natural attenuation (MNA) in groundwater, permeable reactive barriers (PRB), and engineered wetlands.

The effectiveness of MNA for energetic constituents (TNT and RDX) in groundwater was validated at the Louisiana Army Ammunition Plant (AAP), Louisiana, a former explosive-waste disposal lagoon area (ESTCP ER-9518[32]). MNA relies on natural biotic and abiotic processes to reduce the amount of contaminants in groundwater to acceptable levels. This effort produced a draft protocol for the evaluation, selection, and implementation of MNA at explosives-contaminated sites (Pennington et al., 1999). MNA studies also were conducted at Joliet AAP, Illinois. Currently, work to bolster the MNA protocol is being funded by ESTCP (ESTCP ER-0706[33]). New tertiary lines of evidence will be developed and validated at multiple field sites. A software decision tool that can be used to screen sites also will be developed. Project completion is anticipated in FY 2010.

Several types of PRBs are under development to treat and prevent the migration of TNT, RDX, and HMX in groundwater. PRBs are subsurface structures that are created by excavating aquifer material and replacing them with materials that support the degradation of the COCs on contact as the groundwater flows through the barrier. PRBs can be used to intercept groundwater plumes or to isolate source zones that are difficult to remediate. Key issues associated with the use of PRBs include potential loss of system reactivity over time, possible permeability decreases in the barrier, and limitations on the depth to which a PRB can be installed. Projects are ongoing to demonstrate and validate the effectiveness of PRBs containing zero-valent iron for treatment of TNT and RDX (ESTCP ER-0223[34]), organic mulch for RDX and HMX (ESTCP ER-0426[35]), and electrodes (e.g., e^--barrier) for RDX (ESTCP ER-0519[36]). Results from these efforts are anticipated in FY 2008.

Additionally, a SERDP research effort is examining the effectiveness of a combined abiotic/biotic in situ approach to treat TNT, RDX, and HMX in groundwater (SERDP ER-1376[37]). The process combines abiotic degradation of energetic constituents by creating an iron-reducing environment in situ with subsequent microbial treatment of the abiotic reaction intermediates. A project report is expected in FY 2008.

The effectiveness of retention ponds combined with engineered wetlands has been validated for the degradation of energetic constituents in contaminated surface waters and wastewaters (ESTCP ER-9520[38]). Engineered wetlands rely on the use of selected aquatic plants to degrade the energetic constituents. Coupling this technique with the use of retention ponds for collection

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32 http://www.estcp.org/Technology/ER-9518-VFS.cfm.
33 http://www.estcp.org/Technology/ER-0706-Fact-Sheet.cfm.
34 http://www.estcp.org/Technology/ER-0223-FS.cfm.
35 http://www.estcp.org/Technology/ER-0426-FS.cfm.
36 http://www.estcp.org/Technology/ER-0519-FS.cfm.
37 http://www.serdp.org/Research/upload/ER-1376-FR.pdf.
38 http://www.estcp.org/Technology/ER-9520-VFS.cfm.

of surface water has been shown to be effective at reducing energetic constituent concentrations below regulatory limits at the Iowa AAP and Crane Army Ammunition Activity, Indiana. This approach is most applicable when the concentrations of the COCs are high in the surface water and the point of compliance is relatively near the area of use (Larson, 2007).

Uncertainty exists regarding the extent to which natural attenuation of energetic constituents may be occurring in open water bodies. This data gap was identified by the Characterization working group and included as a high priority research need (see Section 3.3.1.1)

No validated treatment technologies for energetic constituents in sediments were identified. SERDP project ER-1431[39] is attempting to assess the potential for underwater degradation and transport of energetic constituents in fresh, brackish, and saltwater environments. Project results should be available in FY 2008.

5.2 Research Needs

5.2.1 Critical Priority

5.2.1.1 Development of Sustainment Approaches to Immobilize or Transform Propellant Constituents Near Firing Points on Small Arms Ranges

There is increasing concern regarding the potential deposition and migration of propellant (e.g., NG) constituents at or behind the firing points on small arms ranges. Firing points are often located near installation boundaries where the potential exists for off-range deposition of the propellant constituents. SERDP project ER-1481[40] is defining the distribution and fate of propellant residues on small arms ranges. The technical report from this project is expected to be published in early 2008. The results of this effort will help determine the requirement for new or modified sustainment approaches for the propellant COCs. Research efforts are needed to determine the effectiveness of currently available sustainment approaches or to develop new methods (e.g., adsorbent or reactive mats) to immobilize or transform propellant constituents deposited near firing points on small arms ranges.

5.2.1.2 Development of Innovative, Wide-Area, Near-Surface Soil Treatment Methods for Impact Areas

The major cause of energetic residue deposition near impact areas is low-order (partial) detonations, which can deposit pure “chunks” of explosive, and the low-order detonation from blowing in place of surface UXO items. Depending on the type of range and munitions used, the areal extent of residue deposition can be quite large and randomly distributed. Research efforts are needed to develop innovative, wide-area, near-surface soil treatment methods for impact areas that are applicable under the range of expected operational constraints.

5.2.1.3 Development of Alternative Explosives to Replace RDX in Testing and Training Munitions and Explosives

RDX is used in large quantities as a secondary explosive in numerous munition items and in demolition explosives (e.g., C4) and is of increasing regulatory concern. Replacing RDX with

[39] http://www.serdp.org/Research/upload/CP-1431.pdf.
[40] http://www.serdp.org/Research/upload/ER-1481.pdf

alternative explosives that have lower environmental risk and performance capabilities equal to or better than RDX would reduce the environmental liability associated with future training exercises. Research is needed to identify or develop substitutes for RDX in munitions and explosives that are as good or better in terms of performance capability.

5.2.1.4 Development of Remote Sensing/Early Warning Monitoring Tools for Detection of Groundwater and Soil Contamination

Soil and groundwater sampling and analysis are costly and often limited by ongoing range activities and conditions. There is a need for remote sentinel monitoring tools to identify and assess the potential for offsite contaminant migration without interfering with ongoing range activities and/or creating an undue risk to personnel. The tools should be able to be applied at locations as close as possible to impact/firing point areas on a range. The results from sentinel monitoring would inform the implementation of mitigation and management strategies. This need was also identified by the Characterization working group (see Section 3.3.1.3).

5.2.2 High Priority

5.2.2.1 Development of Novel Treatment Additives and/or Delivery Methods for Groundwater Treatment and Improved Modeling Capability to Predict Treatment Effectiveness

Once MCs are detected in range area groundwater, technologies are needed to rapidly respond to the risk without significantly impacting range activities. In most cases, soil boring to emplace treatment additives is limited by ongoing activities and/or safety concerns on operational ranges. Technologies that will allow treatment of groundwater without such activities (e.g., soil boring)—either by using existing well networks or alternative emplacement methods—are needed to allow safe and effective treatment of range area groundwater. Research is needed to identify novel treatment additives or methodologies for emplacing treatment additives that avoid the use of boreholes to minimize impact on range activities. Likewise, improved modeling capability is needed to accurately predict treatment effectiveness and, in so doing, minimize the potential impact of the treatment approaches on range activities.

5.2.2.2 Improved Best Management Practices for Disposal of Excess Propellant Bags

Excess propellant bags are typically disposed of by burning near artillery firing positions. This practice may create a source zone of propellant residue. Use of clay lined steel pans in which to burn the bags is preferred, but it is unclear to what extent burn pans are used. Participants identified the need for research to quantitatively assess bag burning operations' potential to generate source zones of contamination (see also Section 3.3.2.1). Depending on the results from this research, there may be a need to develop technologies to remediate the source zones generated by historical bag burning practices and to develop improved BMPs for propellant bag burning to minimize or eliminate the environmental release of propellant residue.

5.2.2.3 Improvements in Munition Manufacturing, Storage, Transport, and/or Deployment Processes to Eliminate or Decrease Dud Rates

A dud is a round that is fired/initiated, but completely fails to function at the target. If the dud round breaks open upon impact or the casing corrodes, it can serve as a source of energetic

contamination. Furthermore, the dud round may subsequently undergo low-order detonation if it is impacted by another munition round. Research into the causes of high dud rates and improvements in munitions manufacturing, storage, transport, and/or deployment processes to decrease dud rates is needed.

5.3 Demonstration Needs

5.3.1 Critical Priority

5.3.1.1 Development of Phytostabilization/Phytoremediation Growing Guides for Varying Geographic and Range Use Conditions

Although the use of vegetation to control erosion and migration of metals is described in currently available BMPs, participants identified challenges associated with the identification of optimum plants for varying geographic locations, range use scenarios, and soil lead concentrations. There is a need to develop guidance on the optimum selection of vegetation to use in small arms range buffer zones, impact areas, and firing lines in varying geographic locations and under varying range use conditions.

5.3.1.2 Development of Improved Guidelines for Small Arms Range Chemical Stabilization Technologies

Chemical stabilization methods (e.g., addition of lime or phosphate to surface soils) are proven to immobilize lead in surface soils. However, work group participants indicated that long-term reliability and determination of optimum application frequency remain an issue with this technology. There is a need for additional guidance for chemical stabilization methods to immobilize lead in surface soils to include methodologies to determine optimum application frequency and long-term effectiveness of amendment additions.

5.3.1.3 Improved Storage, Inspection, and Disposition Procedures for Range Clearance Residue

During range clearance activities, range residue[41] is collected, sorted to remove scrap metal, and transported for disposal. Some range residue items may contain energetic constituents, which could potentially leach into the environment during storage. Research is needed to assess the environmental release of energetic constituents from range residue storage areas. If such areas have the potential to serve as a source term for energetic constituents, effort is needed to develop improved management procedures for the storage and sorting of range residue to minimize the environmental impact of range clearance activities.

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[41] The phrase ‘range residue,’ as used in Section 5.3.1.3 is defined as consisting of practice munitions; residual scrap from expenditure of high-explosive rounds (commonly known as fragmentation, or frag); munitions components, such as cartridge cases, flare canisters, bomb fins, or expended rocket motor casings; target vehicle residue, concrete or lumber from mock targets; and any unnatural materials left by using units of the range (packing material, wooden boxes, metal cans, fiber containers, etc.) (USAF, 2002).

5.3.2 High Priority: Development of Guidance for Transition of Small Arms Range Mitigation/Management Approaches to Single-Site Explosive Ranges

Many mitigation and management approaches currently in practice or under development for small arms ranges and large impact areas have potential applicability at single-site explosive ranges (e.g., OB/OD areas, EOD training ranges). There is a need to validate and transfer mitigation and management approaches in use at small arms ranges and large impact areas for use at single-site explosive ranges, and to develop associated application guidance documents.

6 CONCLUDING THOUGHTS

The sustainability of DoD's operational ranges is crucial to maintaining the readiness of the military forces and developing and testing improved weapon systems. DoD policy states that the design and use of operational ranges and the munitions used on them must minimize potential harmful environmental impacts (DoD Directive 4715.11[42]). Concern over the release of MCs on ranges and their potential to migrate to off-range areas is increasing, however, and endangers the long-term sustainability of ranges.

All Services have established and are implementing procedures to assess the environmental impacts of munitions use on operational ranges (DoD Instruction 4715.14[43]). The Services' assessment programs encompass a variety of ranges (e.g., small arms, artillery, large caliber, mortars, air-to-ground) located in varying geographic, climatological, and hydrogeological conditions. Although assessment programs are being implemented across the Services, mitigation and management approaches for these settings are just now being developed with minimal implementation to date.[44]

There is a need for sound science and effective tools to assess and manage operational ranges in a manner that reduces risk to human health and the environment. Although the state of understanding regarding the release of MCs and their fate and transport in the environment has improved in recent years, it is clear that much remains unknown and that an integrated approach to addressing these gaps is required. Furthermore, improvements in mitigation technologies and long-term sustainable management approaches are needed. SERDP and ESTCP, as DoD programs that promote the development and demonstration of innovative, cost-effective environmental technologies, must determine how their limited funds can be best invested to improve DoD's ability to assess and mitigate existing risks and reduce future harmful environmental impacts from range usage.

Common themes from the three working groups were evident. The lack of quantitative data regarding the source terms on ranges is a key data gap limiting the utility of predictive modeling to determine how and how quickly MCs will migrate in the environment. While the fundamental understanding regarding the release and deposition of MC residue from a variety of munitions has improved, additional research is warranted in several areas to aid in source identification and quantification. These include quantification of MCs released from firing points, OB/OD practices, and bag burning procedures; tools to monitor and track dud and low-order detonations; generation of additional physicochemical data for MCs such as dissolution rates; and tools to locate historical impact areas and firing points.

Much effort recently is being placed on developing improved soil sampling strategies; however, additional outreach is needed to transition such strategies to the user community and to support strategy implementation. The meeting participants generally agreed that research is needed to develop better tools and methods to monitor groundwater and surface water for which sampling methods currently do not exist.

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[42] http://www.dtic.mil/whs/directives/corres/pdf/471511p.pdf
[43] http://www.dtic.mil/whs/directives/corres/pdf/471514p.pdf
[44] With the exception of the sustainable management of small arms ranges for which a number of BMPs have been developed and widely implemented.

Data gaps limiting the ability to perform rigorous risk assessment also were identified. The need for accurate and relevant toxicity data was identified as critical because many of the benchmarks used to define acceptable and unacceptable risk are toxicity-based. Research is warranted to generate additional toxicity data (acute and chronic) and Eco-SSLs for many of the MCs expected to be found on ranges. Improvements in modeling capabilities to predict MC source zone strength and fate and transport of the MCs in the environment are needed. Improved predictive modeling capability would allow for quantitative predictions of the release and migration of MCs to be considered during development of design, use, and long-term management strategies for ranges and impact areas.

Research and validation efforts are needed within the areas of mitigation of MCs in the environment and long-term management strategies for ranges. A number of technologies and management strategies have proven to limit the migration of MCs (primarily heavy metals) from small arms ranges, thus ensuring their long-term sustainment. Effort is needed to evaluate the applicability of these technologies and strategies to other types of ranges. The unique operational constraints of larger ranges (e.g., air-to-ground, artillery) warrant research and validation efforts to develop additional mitigation and long-term management strategies for these sites.

The result of this meeting is a prioritized list of RDT&E needs to guide investments for the assessment, mitigation, and management of operational ranges by SERDP and ESTCP over the next five to ten years.

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Appendix B BACKGROUND PAPERS

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Energetic Munitions Constituents on DoD Training Ranges: Deposition, Accumulation, and Appropriate Characterization Technology

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1. Introduction

The DoD has been concerned with residues of energetic compounds in the environment for well over 20 years. Characterization and subsequent remediation has occurred at many ammunition plants and depots, largely to eliminate sources of ground water contamination from the production, storage, or destruction of either off-specification or out-of-date munitions. The major chemical compounds of concern have been those used as secondary explosives and propellants, the energetic compounds produced and used in the largest quantity. Only in the past 10 years or so, however, has attention been directed at the presence and potential migration of these same chemicals on military training ranges. In response to the concern about these issues, SERDP funded two projects, ER-1155 and ER-1481, to investigate the nature and extent of energetic residues at ranges, and ESTCP has funded a demonstration project ESTCP-0628 to demonstrate and validate the sampling and analysis recommendations from these projects. All three efforts have been collaborative projects of the U.S. Army Engineer Research and Development Center and Defence R&D Canada – Valcartier. The first SERDP project was completed in 2005, the second is scheduled for completion at the end of 2007, and the ESTCP project is to be completed at the end of FY08. Four of the major objectives of these projects were:

(1) to develop an understanding of the types and distribution of energetic residues present at various types of U.S. and Canadian ranges,
(2) to characterize residue deposition from live-fire training, both propellant deposition at firing points and explosives deposition at impact areas,
(3) to develop sampling strategies for collecting representative soil samples at firing points and impact areas that allow an estimate of the mass of residues present, and
(4) to evaluate/modify analytical methods for laboratory characterization of soil samples from training range assessments.

This white paper summarizes the results of these two SERDP projects as well as related results from research sponsored by the Corps of Engineers Distributed Source Program, the U.S. Army Environmental Command (USAEC), the U.S. Army Garrison Alaska, and the Canadian Department of National Defence. This paper emphasizes the energetic compounds used in gun and rocket propellants (excluding perchlorate) and those used as the explosive charges in projectiles, warheads, bombs, and grenades. Our

goal is to provide information needed to develop conceptual site models and sampling strategies in support of the various DoD programs to characterize active ranges, FUDS (Formerly Used Defense) sites, and closed ranges in the MMRP (Military Munitions Response) Program.

Energetic Chemicals

In this discussion, we define energetic compounds as those chemicals used as military secondary (high) explosives and propellants. Most of these chemicals fall into one of three groups – nitroaromatics, nitramines or nitrate esters (Figure 1). Of the nitroaromatics, TNT (2,4,6-trinitrotoluene) is widely used as an explosive, and DNT (2,4-dinitrotoluene) as a component of many single-base propellants. RDX (1,3,5-hexahydro-1,3,5-trinitrotriazine) and HMX (1,3,5,7-octahyrdo-1,3,5,7-tetrazocine) are nitramines used in various explosives, and nitroglycerin (NG) and nitrocellulose (NC) are nitrate esters used in gun and some rocket propellants. Table 1 summarizes the energetic chemicals present in current military explosives and propellants. Some older energetic formulations contain compounds such as tetryl or ammonium picrate, but these compounds are seldom encountered at training ranges.

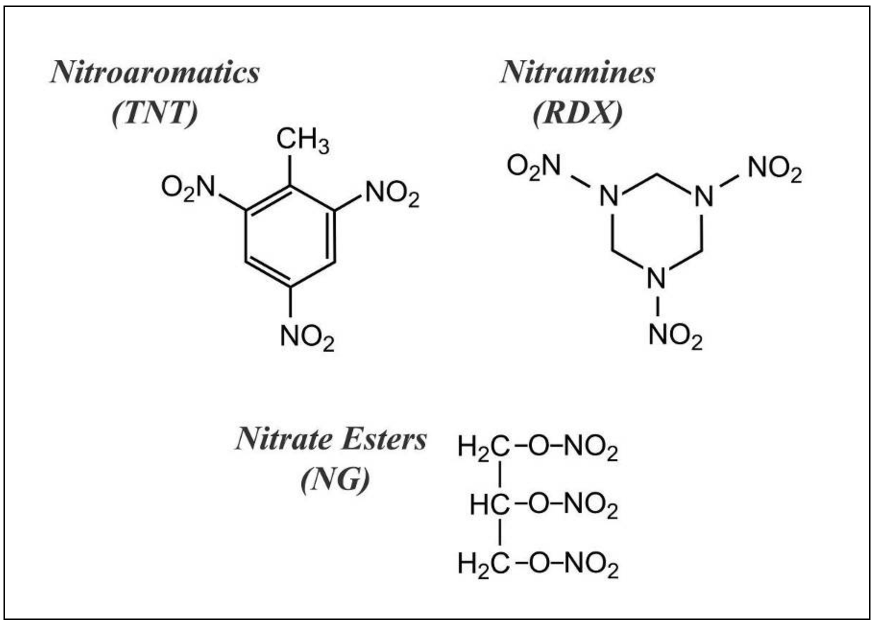

Figure 1. Major classes of energetic chemicals used by the Department of Defense.

Table 1. Energetic chemicals present in military explosive and propellant formulations.

Compound	Uses	Chemical Ingredients
a. Explosive formulations		
Composition B	Artillery; mortar	60% Military-grade RDX (Contains ≈ 10% HMX) 39% Military-grade TNT (Contains ≈ 1% other TNT isomers and DNTs)
Composition C4	Demolition explosive	91% Military-grade RDX
Tritonal	Air Force bombs	Military-grade TNT, aluminum
Composition A4	40-mm grenades	Military-grade RDX
TNT	Artillery	Military-grade TNT
Composition H-6	Air Force bombs	Military-grade RDX and TNT, aluminum
Octol	Antitank rockets	Military-grade HMX and TNT
b. Propellant formulations		
Single-base	Small arms to cannons	NC, 2,4-DNT (e.g. M1, M6); NC, diphenylamine (M10)
Double-base	Multiple applications	NC, NG, ethyl centralite (M2, M5)
Triple-base	Large caliber guns	NC, NG, NQ, ethyl centralite (M30, M31)
Composite	Rockets and missiles	Ammonium perchlorate, Ammonium Nitrate

Important Properties of Energetic Compounds

With the exception of NG, the major energetic compounds are solids at ambient temperatures and are deposited on ranges as particles of the solid material. Although NG is a liquid at ambient temperatures, in its use as a component of double- and triple-base propellants, it is associated with the solid polymeric NC. TNT does not mineralize once exposed to the environment either aerobically or anaerobically, but is environmentally transformed to several isomers of monoaminodinitrotoluene (2ADNT and 4ADNT). These compounds are more mobile in the environment than TNT, but they can chemically bind to natural organic matter in soils and become immobilized. RDX and HMX do not degrade aerobically to any extent in surface soils, and because they do not sorb strongly to soil components, they are the most mobile of the energetic compounds in the environment. RDX and HMX have been found in groundwater aquifers at several training ranges in the U.S. (1,2) and Canada (3).

Energetic compounds are classified as semi-volatile organics, but because many of them are thermally unstable, they are generally not analyzed using gas chromatography. Most analyses of energetic compounds in soil and water are conducted using high performance liquid chromatography (4). Because these compounds are not volatile, soil increments containing these chemicals can be combined and processed without loss due to volatilization, a property that we will exploit when collecting, preparing, and subsampling representative samples (see Section 4).

2. Identity and Distribution of Energetic Residues at DoD Live-Fire Training Ranges

Since 2000 we have conducted field experiments at over 30 military installations in the United States and Canada (Figure 2). The objectives of these studies have been to identify the energetic residues present in the surface soils at various types of live-fire training ranges and to estimate concentrations and distributions of these residues. The major concern is that these residues could serve as sources for off-site migration of various compounds in groundwater or surface water. In addition, these residues could accumulate at concentrations above some risk criteria for target organisms on site.

We have studied a variety of live-fire ranges at U.S. and Canadian bases (5). These include hand grenade, rifle grenade, antitank rocket, demolition, tank firing, mortar, artillery, bombing, demolition, and small arms ranges. Training at these ranges is conducted with different types of munitions that contain a variety of energetic formulations. At most ranges, there is an area where the weapon is fired and a separate impact area where detonations occur. Generally, energetic residues at the firing points are composed of compounds used in propellants, whereas residues at the impact areas are compounds used as high explosives in the munition warheads, or white phosphorus (WP) from smoke rounds. Rather than discussing sampling and analytical methods used to obtain these results here, we defer these discussions until later when the results of characterization research are presented.

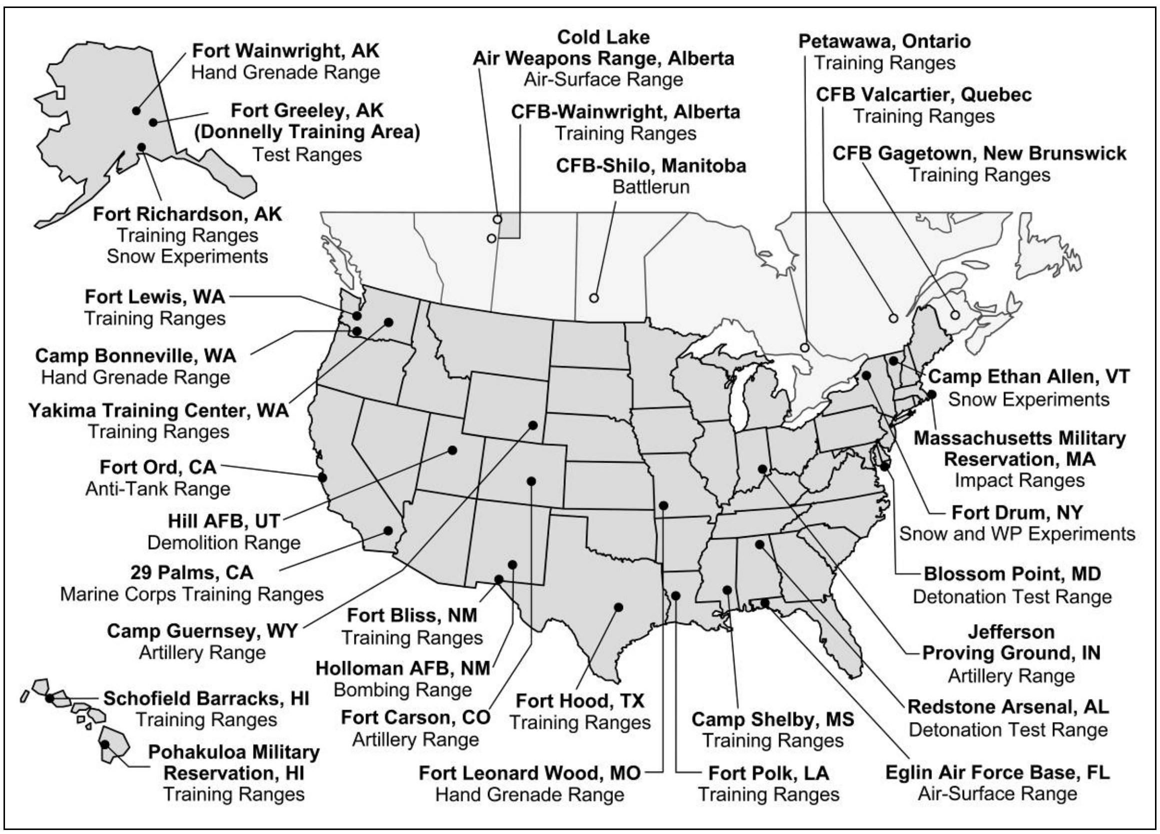

Figure 2. Field experiment sites at various U.S. and Canadian test and training ranges.

Hand Grenade Ranges

Hand grenade ranges are generally only a few hectares in size and, because of the large number of individual detonations in a small area, poorly vegetated. These ranges often have several training bays from which soldiers throw grenades. Most of the detonation craters lie at distances between 15 and 35 m from the throwing pits. Thus only a very small area is subject to residue deposition.

Most training at hand grenade ranges in the United States is with M67 fragmentation grenades. Their explosive charge is 185 g of Composition B. Composition B is 60% military grade RDX, 39% military grade TNT, and 1% wax (Table 1). Military-grade RDX contains about 90% RDX and 10% HMX. Military-grade TNT contains about 99% 2,4,6-TNT and a few tenths of a percent of other isomers of TNT and DNT (6).

Eleven active and two closed hand grenade ranges were studied and fall into two groups (5). One group had concentrations of RDX, TNT, and HMX generally less than 0.12 mg/kg and the other had concentrations of these energetics generally above 1 mg/kg. As will be discussed later, live-fire studies indicate that grenades that detonate as designed (high order) do not deposit sufficient residues to account for these ranges with higher residues concentrations. However, at ranges with higher residue concentrations, we found remnants of grenades that did not completely detonate. These grenades either had undergone partial (low order) detonations or had been duds that were blown in place and did not fully detonate. When these types of detonations occur, much higher residues are deposited accounting for the higher concentrations of residues found at some of these ranges. In most cases the highest concentrations of energetic compounds reside in the top few centimeters of soil.

Antitank Rocket Range Impact Areas

Antitank rocket ranges are direct fire ranges, several hundred hectares in size, and covered with low growing vegetation due to the necessity of maintaining a line of sight for training. Targets are often derelict armored vehicles placed downrange at distances of 100 m or more from the firing points. Weapons fired most often at these ranges are the 66-mm M72 light anti-armor weapon (LAW) and the 84-mm AT4 rocket. These munitions contain M7 double-base propellant; the warhead contains octol. The M7 propellant contains 54.6% NC, 35.5% NG, 7.8% potassium perchlorate, 0.9% ethyl centralite, and 1.2% carbon black. Octol is composed of 70% HMX and 30% TNT. At some ranges practice rounds are fired that contain propellant but do not contain octol. Field experiments were conducted at seven active and one closed antitank rocket range(s) (5). The primary residue detected at the impact areas is HMX; concentrations in surface soils adjacent to targets are generally in the hundreds of mg/kg. TNT, RDX, and two environmental transformation products of TNT (4ADNT, and 2ADNT) are often detectable as well, but the concentrations are always several orders of magnitude lower. HMX concentrations decline as the distance from the target increases. Observations indicate that LAW rockets frequently rupture upon impact without detonating, thereby depositing crystalline explosive over the soil surface. This deposition is thought to be the major source of explosives residues at these impact areas.

Because HMX has a low aqueous solubility (about 4–5 mg/L at 25°C), it tends to accumulate on the surface while the more soluble TNT (about 150 mg/L) dissolves and undergoes environmental transformations. Amino transformation products of TNT can covalently bind to soil organic matter and become immobilized (7). The HMX that slowly dissolves does not strongly interact with soils and can be carried through the vadose zone to underlying groundwater aquifers.

Because antitank rockets are propelled all the way to the target, propellants can still be present when these rockets detonate upon impact. Small pieces of propellant are thereby spread over the soil surface in the area surrounding the targets. These residues can be seen and NG has been detected at the impact areas at concentrations as high as 23 mg/kg.

Sampling conducted at antitank rocket range firing points indicated that in all cases NG was the primary energetic compound present. NG concentrations in surface soil samples from 0 to 25 m behind the firing line are often in the hundreds to thousands of mg/kg, whereas concentrations between the firing line and the target were generally much lower (5).

Artillery Ranges

Artillery ranges are the largest training ranges in the army inventory, covering areas of hundreds of square km. Firing positions are often arranged around the circumference of the range with firing fans leading into the impact areas. In the past, fixed firing points were established, but with more modern mobile artillery, firing activities have become more diffuse as training has evolved to support a “shoot and scoot” strategy. Once fired, artillery and mortar rounds can travel several km before impacting in the general vicinity of targets. The flight path takes these rounds over an area referred to as the safety fan where only a very few rounds impact. Often, this is the largest area of the range. Once the rounds arrive near targets, most rounds are set to detonate upon impact. When the rounds perform as designed, these detonations result in the formation of a crater in the soil, the size being a function of the type of round, the fuse setting and the physical properties of the soil. Rounds that detonate as designed (high order) deposit very little energetic residue. Occasionally a round will impact without detonating, resulting in either a surface or subsurface UXO. On ranges where the soil is rocky or very hard, many of these UXO items can be seen on the surface. In a relatively small number of cases, a round will partially detonate upon impact, resulting in a low-order detonation. In this case, only a portion of the explosive fill is consumed, sometimes leaving a substantial fraction of the explosive fill in or near the ruptured casing.

Many of the artillery ranges have been used for training for many decades. The munitions fired include ordnance currently in the inventory as well as previous ordnance that was used pre- and post World War 2, the Korean Conflict, and Vietnam. Because there has been no uniform management strategy, UXO of a wide array of munitions are present on these ranges and many are still live. The munitions fired to the greatest extent into these ranges are artillery and mortars; a variety of rockets, missiles, and Air Force and Navy bombs have been used as well. Currently the major munition systems being fired into these ranges include 155-mm howitzers, 105-mm howitzers, 120-mm main tank guns, 81-mm mortars, 60-mm mortars, and 120-mm mortars. Other munitions such as 90-

mm recoilless rifle rounds, 4.2-in mortar rounds, 8-in artillery rounds, bombs of various sizes, 40-mm grenades, 106-mm high-explosive plastic (HEP) rounds, 2.75-in LAW rockets, and TOW missiles have also been fired into some of these ranges. These munitions are delivered using single-, double-, and triple-base gun propellants, and rocket and missile propellants. Single-base propellant is composed of NC and 2,4-DNT, double-base propellant is composed of NC and NG, and triple-base propellant is composed of NC, NG and nitroguanidine (NQ). The high explosives used in artillery and mortar warheads are generally either TNT or Composition B, although some older rounds also contained tetryl (methyl-2,4,6-trinitrophenyl nitramines). Smoke-generating munitions contain white phosphorus (WP). Bombs that have been dropped in some of these ranges contain TNT or Tritonal (TNT and aluminum), 40-mm grenades contain Composition A5 (RDX), and LAW rockets contain octol (HMX and TNT).

Artillery and tank range firing points

A number of firing point areas have been sampled at various artillery ranges including firing areas for 105-mm and 155-mm howitzers, various mortars, and 120-mm tank guns (5). The highest concentrations of 2,4-DNT are found at 105-mm firing points. When the concentration of 2,4-DNT in a sample was above 3 mg/kg, we sometimes detected much lower concentrations of 2,6-DNT as well. 2,6-DNT is an impurity in military-grade 2,4-DNT. Soil profile samples indicate that most of the propellant residue is present on the soil surface. Microscopic analysis of the residues indicated that the residues consisted of unburned and partially burned propellant fibers with fiber lengths ranging from 0.4 to 7.5 mm (8).

In other examples, surface soil samples were collected at a multi-purpose range complex in front of a fixed firing point for 120-mm tank guns. Both 2,4-DNT and NG were detected at 75 m, the farthest distance from the firing point sampled. Soil samples collected at 155-mm firing points, however, had much lower residue concentrations, often below analytical detection limits.

Artillery ranges away from impact areas and firing points

At several installations, the U.S. Army Environmental Command (AEC) and the U.S. Army Center for Health Promotion and Preventive Medicine (CHPPM) conducted Regional Range Studies to assess the overall environmental impacts of residues from firing activities on artillery ranges (9,10). Similar studies were conducted by the Defence Research Establishment-Valcartier (11,12). Because target areas represent only a small fraction of the total area of artillery ranges, many of the areas sampled were quite a distance from any recognizable target. Most of these samples did not contain detectable energetic residues indicating that most of the total area at these ranges is virtually uncontaminated.

Artillery range target areas

Because target areas receive the largest number of detonations, we collected samples around targets at many of the artillery ranges visited. These targets are generally

derelict trucks, tanks, and armored personnel carriers; many have sustained enormous damage after years of target practice. Because of the danger of encountering buried UXO items, and the fact that most detonations scatter residue over the surface, most of the soil samples from these areas were collected from the surface.

Overall, the concentrations of energetic compounds near artillery targets are low and a defined concentration gradient is not apparent, unlike that found for antitank range target areas (5). Surface soil samples from some targets can have concentrations in excess of one mg/kg, but the concentrations at most targets are less, sometimes below the detections limits of the analytical methods used.

Artillery ranges near low-order (partial) detonations and detonation craters

By far the highest concentrations of energetic residues that we encountered at artillery ranges were associated with rounds that had undergone a low-order detonation (5). In most cases, chunks of pure explosive were observed on the soil surface near these items and concentrations of energetic compounds in the surface soil (particles <2 mm) were up to the percent levels. The areas influenced by these low-order detonations were explored in several cases, but this remains an important research topic and no generalizations in this regard are currently possible. We also collected a series of samples at several installations to determine the residual concentrations of energetic compounds within impact craters and around their perimeter. Overall, areas in and near detonation craters and intact UXO items are not heavily contaminated with residues of energetic compounds. However, the destruction of UXO items with C4 demolition explosive can sometimes result in a substantial increase of energetic compound concentrations in the near vicinity of the detonations, particularly when they result in a low order detonation of the item being destroyed.

Bombing Ranges

Air Force bombing ranges are very large, generally hundreds of square kilometers in size, but the areas currently used for training with high-explosives-containing bombs is much smaller, generally only tens of hectares. We sampled two live-fire bombing ranges, (13,14,15) and several artillery ranges where bombing with HE-containing bombs had taken place (16).

The high explosive present in U.S. and Canadian Air Force bombs is usually tritonal (TNT, aluminum powder). Some older bombs contained TNT alone. While experiments documenting the residue deposited when a bomb detonates as designed have not been conducted, experimental results for large artillery rounds indicate that large mass HE detonations are very efficient, dispersing only microgram to milligram quantities of residue when they detonate high order (see below). As with other munitions, low-order detonations are the major source of residues from bombs. Communication with range personnel indicates that low-order bomb detonations generally occur several times per year. A low-order bomb can deposit kg quantities of residues as chunks and soil size particles. We observed the presence of several low-order bombs in our on-site research.

Results for soil samples collected at Air Force bombing ranges indicates that high concentrations of TNT (hundreds of mg/kg) are found in the immediate vicinity of low-order bombs that contain tritonal, but soils concentrations elsewhere are much lower. The

mono amino transformation products of TNT (2ADNT and 4ADNT) are also found but at much lower concentrations. RDX has been detected at low concentrations (generally less than 0.1 mg/kg) and its presence may be due to the use of C4 demolition explosive (91% RDX) to destroy duds.

Navy bombs contain H-6 as the main explosive charge. H-6 is composed of RDX, TNT and aluminum and is used because it is considered safer for on-ship storage. We sampled one range where H-6 bombs were dropped (16). At least one bomb had apparently undergone a low-order detonation. In this area we observed chunks of H-6 and the mean concentrations of RDX, TNT, and HMX in a 100-m X 100-m area just down slope of where the largest mass of explosive was observed were 9.4, 1.4, and 1.3 mg/kg, respectively.

Demolition Ranges

Military explosive ordnance disposal (EOD) technicians use demolition ranges at active DoD training facilities to destroy duds of various munitions that are considered safe to move. Sometimes chunks of high explosive or unused propellants are also destroyed at these ranges either by detonation or burning. Demolition ranges are generally only a few hectares in size and sparsely vegetated near demolition craters. Demolition craters are often used many times before being filled in. At active installations, a quantity of C4 explosive is generally placed on the item and detonated using a blasting cap, eliminating any detonation hazards from these items. At some Air Force and Navy demolition ranges, C4 explosive is used to blow a hole in practice bombs to ensure they contain no high explosives before they can be removed from the range for recycling.

We generally found RDX and HMX in surface soils at the demolition ranges we sampled, presumably from the use of C4 demolition explosive (17). Concentrations were generally in the low mg/kg range. Pieces of C4 are often observed on the surface at demolition ranges, and unlike other ranges, they are present in the subsurface soil as well. RDX concentrations in the groundwater near the demolition range at the Massachusetts Military Reservation were the highest found at the installation (1).

Other energetic compounds such as TNT, NG and 2,4-DNT are also often detected in soils at demolition ranges, but generally at lower concentrations than RDX. NG and 2,4-DNT are present due to burning of excess propellants at these ranges.

Small Arms Range Firing Points

In the past, sampling at small arms ranges has been conducted for lead (and more recently tungsten), generally at backstops and berms. In 2006 we sampled at several small arms firing points at two installations (18). Surface soil samples collected just in front of the firing positions revealed the presence of NG at concentrations in the low to hundreds of mg/kg. Additional research on this topic is underway in SERDP Project 1481.

3. Residue Deposition Studies

A series of experiments were conducted to understand the mass of energetic residues deposited when rounds are fired at firing points and detonate at impact areas. Because of potential problems with the presence of residues from past detonations, the difficulty in identifying the footprint of residue deposition on soil, and the need to collect large surface area samples to make these measurements, many of these studies were conducted at snow-covered ranges (19).

The mass of propellant residues deposited was studied for artillery and mortar firing (20-23) and for the various military small arms (24). Surface snow was collected and the mass of NG and/or 2,4-DNT was determined in both the snowmelt and the filtered soot present in the snow. The total mass of these residues on a per-round-fired basis is presented in Table 2. The very small amount of residue produced from firing the 155-mm howitzer was surprising, but these results are consistent with the very low concentrations found for soil samples collected at 155-mm firing points. Conversely, residue deposition from small arms firing was large, but not surprising from earlier forensic analysis of clothing after handgun firing (25). Because large numbers of these round are fired at small arms training ranges, substantial accumulation of NG at these ranges is probable.

Table 2*. Mass of NG or 2,4-DNT deposited per round fired for various weapon systems.

Weapon System	Propellant	Constituent	Rounds fired	Residues/ round (mg)
Howitzers				
105-mm	M1-I & II	DNT	71	34
155-mm	M1	DNT	60	1.2
Mortars				
81-mm	M9	NG	61	1,000
120-mm	M45	NG	40	350
Small Arms				
5.56-mm Rifle	WC844	NG	100	1.8
5.56-mm MG	WC844	NG	200	1.3
7.62-mm MG	WC846	NG	100	1.5
9-mm Pistol	WPR289	NG	100	2.1
12.7-mm MG (.50 cal)	WC860 & WC857	NG	195	11

* Information from Walsh et al. (in press). (26)

The mass of explosives residues deposited when a round detonates high order was estimated for hand grenades (24), mortars (21, 22, 26), and artillery rounds (20-23). A summary of the estimated deposition per round detonated high order is provided in Table 3. Overall, the consumption of the high explosives present in the warheads of these rounds is always greater than 99.99%; thus the mass of residues deposited is quite small when rounds detonate as designed.

Low-order detonation tests were conducted at Blossom Point, Maryland (27). Detonations were conducted on a raised table and the mass of energetic compounds deposited was obtained after recovery from tarps covering the surrounding area. Five types of munitions were studied: 60-mm, 81-mm, and 120-mm mortars containing Composition B, 105-mm howitzer projectiles containing Composition B, and 155-mm howitzer projectiles containing either TNT or Composition B. Table 4 summarizes the results of this work with percent of original mass of explosives deposited ranging from 27 to 49%. This is an enormous mass of residue compared with that deposited from high order detonations (Table 3). For a rule of thumb, it takes about 10,000 to 100,000 high order detonations to deposit the same mass of residue as that from one low-order detonation of the same type of munition. Clearly from a management perspective, it is these low-order detonations that constitute the main source of explosives residues at impact areas.

Table 3. Mass of explosives residue deposited from high-order detonations.

Weapon System	Explosive	Mass deposited (μg)	Rounds fired	Percent deposited
Mortars				
60-mm	RDX	94	11 (22,24)*	3×10^{-5}
81-mm	RDX	8500	5 (24)	2×10^{-3}
81-mm	TNT	1100	5 (24)	3×10^{-4}
120-mm	RDX	4200	7 (21)	2×10^{-4}
120-mm	TNT	320	7 (21)	2×10^{-5}
Hand grenade				
M67	RDX	25	7 (24)	2×10^{-5}
Howitzer				
105-mm	RDX	95	9 (23)	7×10^{-6}
105-mm	TNT	170	9 (23)	2×10^{-5}
155-mm	RDX	310	7 (20)	5×10^{-6}

Table 4. Mass of explosives residue deposited from low-order detonation tests (from Pennington et al. 2006, Table 9-1).

Ordnance item	Explosive fill	Mass of explosive in round (g)	Percent deposited
Mortars			
60-mm	Composition B	191	35
81-mm	Composition B	726	42
120-mm	Composition B	2989	49
Howitzer			
105-mm projectile	Composition B	2304	27
155-mm projectile	TNT	6985	29

4. Site Characterization Research

The major objectives of our site characterization research were: (1) to evaluate alternative soil sampling strategies to ensure that samples collected would be truly representative of training range firing points and impact area soils, and (2) to assess/modify laboratory sample processing and analysis protocols for accurate and precise determination of residue concentrations in these soil samples.

Soil Sampling Studies

Site characterizations for environmental assessments have generally used what is commonly referred to as the grid-node sampling strategy. Using this strategy, the area of interest is divided into a number of individual grids, the size of each being a function of the total area to be assessed. Within each grid, one (or perhaps several) discrete sample(s) is collected and shipped to an offsite contractor laboratory where samples are processed and analyzed. The results of these analyses are assumed to be representative of concentrations within the grid and also assumed to be normally distributed because the numbers of samples are insufficient to assess the actual data distribution. The assumption that these discrete samples are "representative" of analyte concentrations within the grid is generally not tested, although the concentrations determined for discrete samples collected from within the same grid often do not agree.

Because earlier research had indicated that concentrations in discrete samples can vary substantially even over short distances for explosives residues (28, 29), and because energetic residues are deposited at training ranges as discrete particles (30, 31), we were concerned about using the grid-node sampling strategy employing discrete samples to represent grids at firing points and impact areas. To test just how diverse individual discrete samples might be from within these areas, experiments were conducted at firing points and impact areas at several different training ranges. In most cases, a 10-m × 10-m grid was established and was subdivided into 100 1-m × 1-m cells. A discrete sample was collected from within each cell and analyzed for energetic compounds according to established protocols (4).

The major analyte detected in seven different grid areas at six different installations varied from 2,4-DNT and NG at firing point areas to RDX, TNT and HMX at impact areas (Table 5). The maximum to minimum ratios varied from over two orders of magnitude to almost five orders of magnitude for these sets of 100 values, indicating that discrete samples could not provide reliable estimates of mean concentrations within grids as small at 10-m × 10-m. In fact, the maximum and minimum concentrations among nine discrete samples collected within a single 1-m × 1-m cell varied by two orders of magnitude, demonstrating the magnitude of very short-range heterogeneity in these areas. The median values for the hundred discrete samples within each data set were always less than the mean, and the standard deviations were always equal to or greater than the means, indicating that in no case were the concentration estimates from discrete samples normally distributed.

Table 5. Variability of soil concentrations among 100 discrete samples collected within 10-m x 10-m grids at various training range impact areas.

Installation	Area*	Range type	Analyte	Concentration (mg/kg) Max	Min	Median	Mean	Std dev.
Donnely Training Area (AK)	FP	Artillery	2,4-DNT	6.38	0.0007	0.65	1.06	1.17
CFB-Valcartier (QC)	FP	Antitank rocket	NG	2.94	0.02	0.281	0.451	0.494
CFB-Valcartier (QC)	IA	Antitank rocket	HMX	1150	5.8	197	292	290
Holloman AFB (NM)	IA	Bombing	TNT	778	0.15	6.36	31.8	87.0
Ft. Polk (LA)	IA	Mortar	RDX	2390	0.037	1.7	71.5	315
Cold Lake (AB)	IA	Bombing	TNT	289	0.38	6.57	16.2	32.3
Ft. Richardson (AK)	IA	Artillery	RDX	172	<0.04	<0.04	5.46	24.8

* Firing point (FP) or Impact Area (IA).

Another approach we investigated was the use of multi-increment samples to estimate mean concentrations within grids. In this case, instead of collecting and analyzing single point samples, samples are built by combining a number of increments of soil from within the grid of interest to obtain a mass of sample of about 1 kg. These samples can be collected in a totally random fashion or more systematically. A series of sampling experiments were conducted at a variety of training range firing points and impact areas. Some of the areas sampled were identical to those where discrete samples were employed. The variability among replicate multi-increment samples was much lower than found for discrete samples within the same sample grids (Table 6). For example, 2,4-DNT concentrations in discrete samples collected with a 10-m × 10-m firing point area at Donnelly Training Area ranged over almost four orders of magnitude whereas concentrations among the ten replicate multi-increment samples from this area varied by only a factor of less than three. Similarly, the range in RDX concentrations for discrete samples from a 10-m × 10-m grid at a Ft. Polk impact area varied by nearly five orders of magnitude; the range for multi-increment samples was reduced to less than two orders of magnitude.

Table 6. Variability of soil concentrations among multi-increment samples collected within grids at various training range impact areas.

Installation	Area*	Range type	Increments / Sample	Replicate Samples	Grid Size	Analyte	Max	Min	Mean	Std dev.	Median
Donnely Training Area (AK)	FP	Artillery	30	10	10 m x 10 m	2,4-DNT	1.35	0.60	0.94	0.24	0.92
Holloman AFB (NM)	IA	Bombing	100	3	10 m x 10 m	TNT	17.2	12.5	14.4	2.45	13.5
Ft. Polk (LA)	IA	Mortar	25	10	10 m x 10 m	RDX	290	4.6	54	86	25
29 Palms (CA)	IA	Artillery/ Bombing	100	6	100 m x 100 m	RDX	9.4	3.9	5.6	2.1	4.8
Hill AFB (UT)	DA	Thermal treatment	100	3	100 m x 100 m	HMX	4.26	3.96	4.13	0.15	4.16

* Firing point (FP), Impact Area (IA), or Demolition Area (DA).

Grid sizes up to 100-m X 100-m were sampled using the multi-increment approach. Triplicate samples varied from 3.9 to 9.4 mg/kg for RDX for soil samples from an impact area at 29 Palms, CA (16) and from 3.96 to 4.26 mg/kg for HMX for samples from a thermal treatment area at Hill AFB (32). Overall, multi-increment samples provided reliable estimates of mean concentrations within grids at firing point and impact areas. The number of increments in each sample varied from 30 to 100, depending on the grid size being characterized and the amount of chunks of pure energetic compound observed on the surface (33). In addition, data from replicate multi-increment samples were found to be normally distributed in most cases whereas the data distribution of discrete samples was always non-normal. We recommend that multi-increment samples be collected using a systematic-random pattern rather than a totally random pattern that sometimes over or under represents various areas of the grid. In the systematic-random pattern, a random starting point is selected and increments are gathered on an even spacing as the sampler walks back and forth from one corner of the grid to the opposite corner.

Sample Processing and Analysis

Since the early 1990s, energetic compounds in soil samples have been analyzed using USEPA standard methods SW846 Method 8330 (4) and Method 8095 (34). The sample processing and analysis steps in these methods were developed to support the Installation Restoration Program, mainly for characterizing soils at ammunition plants and depots (35, 36). The deposition of energetic residues at training range firing points and impact areas is quite different than that at ammunition plants where deposition was largely due to disposal of wastewater containing high concentrations of secondary explosives. Thus the target analytes in Method 8330 were limited to the major secondary explosives, their manufacturing impurities, and environmental transformation products. The concerns about spatial heterogeneity in deposition were different than those for training range samples and the disposition of the residues within the soil samples is quite different as well. A major objective of the SERDP-sponsored programs and those sponsored by USAEC and the U.S. Army Garrison Alaska was to assess the applicability of Methods 8330 and 8095 to soil samples from ranges.

Once samples arrive at commercial laboratories, common practice has been to remove a small portion of the sample for air drying. The remainder of the sample (often greater than 90%) is never processed. Any replicate analysis also comes from the same small portion that was removed and air dried. In training range samples, the analytes are largely present as particles of propellant or explosive and a large amount of heterogeneity exists within soil samples sent to the laboratory; concentrations in replicate subsamples can have concentrations differing by a factor of ten or more (37). To minimize this source of uncertainty, the entire sample must be air dried and mechanically ground to reduce the particle size of the energetic residues present in the sample (37).

Other changes that have been found to improve analyses for training range soils includes, increasing the sieve size from 30-mesh (< 0.595 mm) to 10-mesh (< 2.0-mm) to include a portion of the particle size fraction that often contains energetic compounds, using10-g subsamples and extraction with 20-ml of acetonitrile, allowing the use of extraction on a table shaker as well as in an ultrasonic bath, and including NG as a target analyte for the method (38). These changes have been incorporated in a new method,

SW846 Method 8330B (39), which is recommended for training range soil analyses. This method also includes a sampling appendix in which the recommended systematic-random multi-increment sampling strategy is described.

5. Summary and Conclusions

The types of residues, their concentrations, and distributions differ depending on the type of range and munition used. For hand grenade ranges, the major residue deposition occurs when grenades undergo a low-order (partial) detonation, either when thrown or when duds are blown in place using C4 explosive. The major energetic residues on these ranges are RDX and TNT from Composition B, the explosive charge in M67 and C13 fragmentation grenades. For ranges where a recent partial detonation has occurred, concentrations are generally in the low mg/kg range and the distributions are more spatially homogeneous than at other types of ranges due to the thousands of individual detonations that continuously redistribute the residue. Multi-increment samples consisting of 30 increments generally have been found to be adequate for obtaining representative samples of surface soils at hand grenade ranges.

At antitank rocket ranges, the major residue present in surface soils at the target area is HMX from the octol used as the high explosive in the warhead of 66-mm M72 LAW rockets. A concentration gradient is present in surface soils relative to the distance from targets. HMX concentrations in surface soils near targets are generally in the hundreds to low thousands of mg/kg with TNT concentrations about one-hundredth that of HMX. The high levels of HMX in the soil at antitank rocket ranges can be attributed to the high dud and rupture rate of the M72 rockets and the low solubility of HMX. Short-range spatial heterogeneity in residue concentrations at these sites is high, and in order to get representative samples, it is necessary to take multi-increment samples of at least 30 increments.

At the firing points of antitank rocket ranges, NG is present from the double base propellant used in the 66-mm M72 rockets. The major deposition of residue is behind the firing line due to the back blast from this weapon. Concentrations as high as a tenth of a percent have been found in soil up to 25 m behind the firing line. NG is also found between the firing line and the target, but concentrations are generally several orders of magnitude lower than behind the firing line. Multi-increment samples have been found to provide adequate characterization for samples from impact areas and firing points at antitank rocket ranges. Because the residues in these samples are largely present as fibers or slivers of propellant, samples must be processed using larger sieves (10-mesh, 2-mm) than recommended in SW-846 Methods 8330 and 8095. We also recommend thorough grinding of samples using a mechanical grinder prior to subsampling to preserve the representativeness of the portion to be used for extraction and analysis.

Most of the acreage at artillery ranges remote to firing points and targets is uncontaminated with residues of energetic compounds. At artillery and mortar firing points, the energetic residues are usually either 2,4-DNT or NG, depending on the type of propellant used for the specific firing platform, and residues can be deposited at distances up to 100 m ahead of the muzzle. For 105-mm howitzers, the major detectable residue is 2,4-DNT, which can accumulate into the mg/kg range for fixed firing points. The residues from the single-base propellant used with this weapon are distributed primarily as partially burned or unburned propellant fibers. Residue deposition and accumulation

from 155-mm howitzers are much lower than that from 105-mm howitzers. NG deposition from mortars is primarily NG from double-base propellants. Propellant residues are deposited at the soil surface and the highest concentrations remain at the surface unless the soil is disturbed. Propellant residues from mortars are greater than those from artillery.

Near targets at impact ranges, the majority of munitions detonate high-order, and they appear to deposit very little residue. The major energetic residue deposition is due to low-order (partial) detonations, which can deposit chunks of pure explosive. Residue concentrations of hundreds or thousands of mg/kg are often found in the surface soils next to these detonations. The major residues are TNT and RDX from military-grade TNT and Composition B, the major explosives used in mortar and artillery rounds. The distribution of residues in the area of the range where detonations occur is best described as randomly distributed point sources. Some of these point sources may be due to low-order detonations from blowing in place of surface UXO items. At present the detection of these point source areas has been visual, but some initial research has been conducted to try to develop a near-real-time detection capability for these zones. The collection of representative samples in areas subject to these partial detonations is a major challenge, and approaches utilizing multi-increment sampling have not been adequate.

6. Remaining Data Gaps and Recommendations for Future Research

Over the past 5 years, enormous progress has been made in developing an understanding of the nature of energetic residues on training ranges. Even so, some data gaps remain on the rate of dissolution and fate of energetic compounds. Also, practical mitigation methods based on the distribution of residues need to be developed for large training ranges. The following is a brief description of future research that could fill some of these data gaps.

Residue Deposition and Dissolution

In terms of mass of residues deposited, explosives residues from low-order detonations and propellant residues at firing points are the major depositional events. Research has revealed the physical nature of this deposition for explosives from low-order detonations and propellant residues from single-base and double-base propellants. To date, no experiments for triple-base propellants containing nitroguanidine have been completed.

Dissolution for explosives and release of propellant components from the polymeric nitrocellulose matrix are the first steps in transport of energetic residues off site, either vertically into groundwater aquifers or horizontally in overland flow runoff (40). On-going research is addressing the rate of dissolution for explosives of various types (SERDP ER-1482), and some initial experiments are underway to investigate the release of nitroglycerin from 105-mm, 5.56-mm, AT-4,and 81-mm illumination propellant. Additional studies are needed to address the rate of release of nitroglycerin, 2,4-DNT, and nitroguanidine from propellant residues as a function of particle size. This data is critical to any realistic mathematical modeling of the fate of these components on ranges.

Field experiments have been conducted to estimate the explosives residue deposition from high-order detonations of a number of munitions to include hand

grenades, mortars, artillery, and some shoulder-fired rockets. Additionally, experiments have been completed to estimate propellant residue deposition from firing of various munitions to include small arms, mortars, artillery, and some initial studies with shoulder-fired rockets. These data allow estimation or residue deposition as a function of rounds fired. Some data gaps remain including propellant residues from AT-4 rockets and propellants from Navy munitions.

Fate of Nitroglycerin

It appears that propellant residues containing NG are common at many small-arms range firing points (18). Column experiments conducted under saturated conditions show that NG migrates rapidly through soils, yet NG has not been observed in ground water samples to any extent, even at the Massachusetts Military Reservation (18). The two isomers of dinitroglycerin have been identified in soil samples that have large concentrations of NG, but it is not clear whether these are manufacturing impurities, environmental degradation products, or both. Additional field studies, including emplaced lysimeters, and column studies conducted under unsaturated conditions are necessary to identify fate processes that appear to mitigate NG transport.

Demolition Ranges

Demolition ranges can be a very large source of energetic residues, and probably other munitions constituents as well. While characterization of other ranges is predominantly a two-dimensional problem because the residues are deposited on the surface, this is not true for demolition ranges. Here particles and chunks of C4 demolition explosive can be found several meters below surface and the best method for collection of representative samples to estimate the source mass has not been fully developed.

Wide Area Assessment

Because the largest source of explosives residues are areas where low-order detonations have occurred or where surface UXO have been ruptured by nearby detonations, it is these occurrences that must be located if remedial activities are to be successful in reducing the mass of residues present on ranges. In some cases these areas can be visually located, but in areas with dense vegetation or areas that are inaccessible due to UXO, this will not be possible. Impact areas are often quite large and it is not practical to try to identify areas where these events have taken place by large-scale soil sampling activities. A more attractive option is the use of some screening approach to eliminate areas where these events have not occurred so that a more intensive effort can be made in areas where residues are present. One option to address this problem is to consider the use of sensors that have been developed for detection of land mines or improvised explosive devices. Mounting of a sensor on a robotic platform is a particularly attractive option for areas that are extremely hazardous such as areas with 40-mm grenades or submunitions. The mass of explosives present at ranges is much greater and easier to detect than battlefield IEDs or land mines.

Additional Characterization Experiments

Several additional field and laboratory experiments should be conducted to determine the minimum number of increments and sample mass to adequately characterize areas with low-order detonations.

Realistic Remedial and Range Management Approaches

While a number of alternative approaches have been considered to alleviate residue issues at ranges, many do not consider issues associated with restricted access and the fact that explosives residues are present in impact areas as distributed point sources. In addition, better disposal practices for excess propellant from firing activities need to be developed and implemented.

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Near- and Long-Term Range Management Strategies: Sustainable Use of HE on Operational Testing and Training Ranges

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I. Introduction and Background

The sustainability of live fire ranges is of paramount importance to ensure continued training at army installations. Active military ranges are crucial to military readiness, and the development of effective treatment options for energetic contaminants is essential for range management and sustainability (Borthwick and Beshore, 2000; Jones et al., 2002). The munition components considered in this paper are found primarily at impact areas and firing lines of testing and training ranges and usually consist of a mixture of residues from several energetic compounds. These include the nitroaromatic explosive compounds 2,4,6-trinitrotoluene (TNT), 2,4- and 2,6-dinitrotiluene (DNT), and trinitrophenylmethylnitramine (tetryl), the nitrate esters, cellulose trinitrate (nitrocellulose, NC) and pentaerythritol tetranitrate (PETN), and the nitramine compounds, hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). Several of the energetic compounds have been in use for decades either as a primary explosive or in mixtures, favored because of their shelf-life, stability, and effectiveness. These characteristics are compared in Table 1.

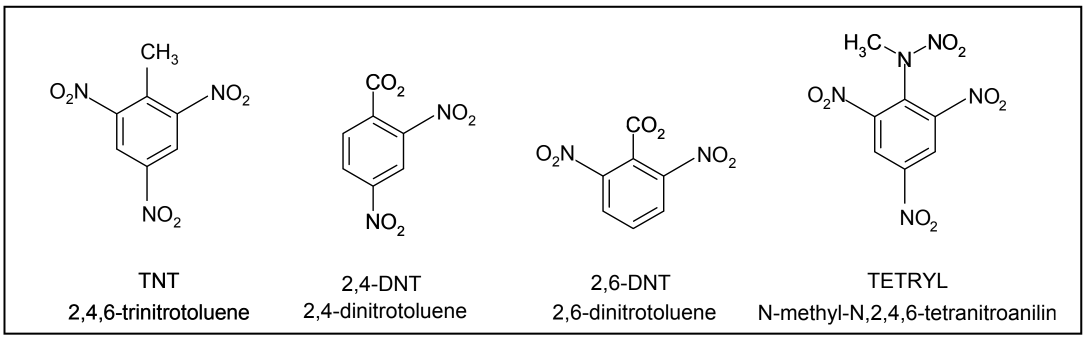
Table 1. Comparison of militarily significant parameters of munition constituents.

HE	Safety	Insensitivity	Lifespan	Effectiveness
TNT	4	1	5	5
DNT*	4	1	5	N/A
Tetryl	4	1	5	5
RDX**	4	1	5	N/A
HMX**	4	2	5	N/A
NC	4	2	3	5
PETN	4	1	5	5

* Impurity occurring in nitration of toluene (to produce TNT). Also a classic exudate in TNT-filled UXO.
** Explosive ingredient

Several chemical and physical characteristics of these energetic compounds are summarized as these affect the selection of range management strategies. The structures of the three chemical classes of energetics under discussion are shown in Figure 1; Figure 1A is the nitroaromatic compounds, Figure 1B is the nitramine compounds, and Figure 1C is the nitrate esters. Physical characteristics of these compounds that affect their environmental fate and transport, and, therefore, their management on ranges, are summarized in Table 2.

A



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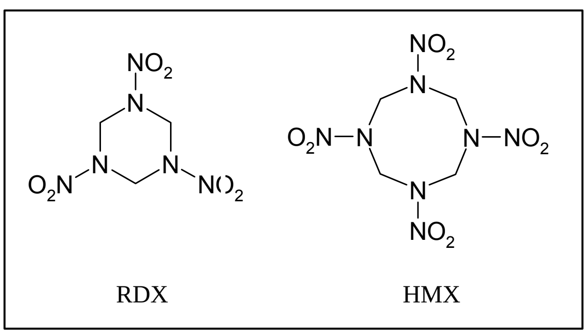

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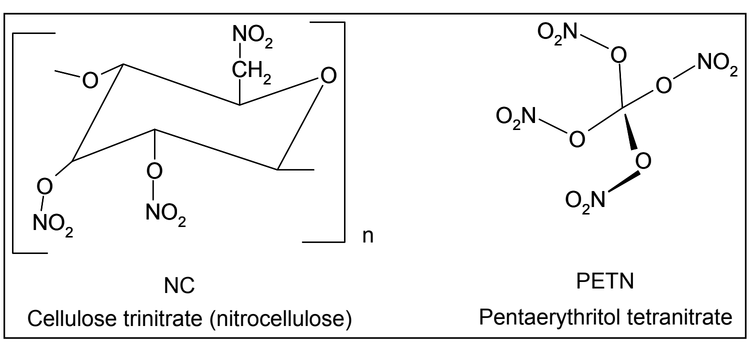

Figure 1. Chemical structures of relevant energetic compounds. A. Nitoaromatics. B. Nitramines. C. Nitrate esters.

Table 2. Selected characteristics affecting fate and transport of energetic compounds found on testing and training ranges[a]

Compound	Aqueous solubility (mg/L)	Log K_{ow}	Log K_{oc}	K_d (L/Kg)
TNT	88.5 at 20 °C	2.2	3.2	0.04–413[c]
2,4-DNT/2,6-DNT	280 at 25 °C	95 at 25 °C[b]	1.79-2.4[c]	0.09–7400[c]
	259 at 25 °C	78 at 25 °C[b]	1.79-1.89[c]	0.96-125[c]
Tetryl	80 at 25 °C	250 at 25 °C[d]	3.1-3.5	ND
RDX	59.9 at 25 °C	0.87	0.88-2.4[c]	0.06 – 8.4[c]
HMX	5 at 25 °C	0.226	2.8	0.12 – 17[c]
NC	ND	ND	ND	ND
PETN	2.1 at 25 °C	4500 at 25 °C	3.39	ND

[a]all values extracted from McGrath (1995) and Brannon and Pennington (2002) unless noted otherwise
[b]Rosenblatt et al. 1991
[c]value depends on the soil characteristics
[d]Agency for Toxic Substances and Disease Registry (ATSDR)-tetryl 1999
ND – not determined

Because of its ubiquitous use as a military and industrial explosive in many nations, TNT is a well-characterized explosive. A byproduct of TNT production, DNT has been used in explosives as a component of Composition C series, particularly C3. C-3 is composed of RDX (77%), DNT (10%), MNT (mononitrotoluene – 5%), TNT (4%), Tetryl (3%) and NC (1%). While Composition C3 is no longer being used as a gun projectile main charge, some stocks may still be in service. Tetryl has been used in a number of explosive formulations. Besides being used as an ingredient in the above mentioned Composition C series explosives, tetryl is also the primary explosive in tetrylols (80% tetryl, 20% TNT). Tetrylols were used as a base charge in detonators (Gibbs and Popolato, 1980). Since 1980, tetryl has largely been replaced by RDX (Gibbs and Popolato, 1980; Jenkins and Walsh, 1994).

RDX is normally used as a mixture with other explosive ingredients or plasticizers. In this way, RDX forms the base for the common military explosives such

as Composition A (RDX plus wax), Composition B (RDX plus TNT), and Composition C (RDX plus non-explosive plasticizer). HMX explodes violently at high temperatures (534°F and above) and, because of this property, it is used in nuclear devices, plastic explosives, rocket fuels, and burster chargers. A small amount of HMX is formed as a by-product in the manufacture of RDX so it always appears as a co-contaminant with RDX. Pennington et al. (2001, 2002) reported both concentric concentration patterns roughly centered on impact craters and also detectable levels of explosives on soil surfaces at points widely separated from the impact crater. When the RDX was completely detonated, the concentrations on the surface were low, ranging from 0.5 to 1.0 mg/kg. However, incompletely detonated charges (low-order) formed a point source in the soil, some of which had concentrations as high as 1.5%.

Nitrocellulose is a nitric acid ester of cellulose (a glucose polymer) and is used in a number of military and commercial explosive compositions. PETN is the most stable and least reactive of the explosive nitric esters. It is also one of the most powerful. It is used in high-efficiency detonators, detonating cords, and to produce boosters or bursting charges in small caliber ammunition, and in land mines and shells. Because PETN can also be incorporated into gelatinous, industrial explosives, it is also used in making plastic explosives. Besides datasheet, PETN is also incorporated into pentolite (PETN and TNT) and semtex.

Adsorption to Soil

Soil adsorption coefficients for TNT vary over a range of 0 to 11 L/kg (Brannon et al. 1999; Pennington and Patrick 1990). Adsorption coefficients onto homoionic clays ranged up to 413 L/kg and followed a Freundlich rather than a linear isotherm model (Price et al. 2000). The combination of a high, but reversible, sorption coefficient, the high water solubility of TNT (Table 2), and the magnitude of contamination at many sites, results in a high potential for continuous percolation of contaminated water from surface and near-surface sources through the unsaturated zone to the groundwater. Values for adsorption of the dinitrotoluenes to aquifer soils were consistent with K_d values for other energetics, i.e., typically <1 L/kg (Pennington et al. 1999). Values for adsorption to pure clays were higher for 2,4DNT than for 2,6DNT (Haderlein et al., 1996). While the K_d for tetryl has not been determined, its through soil may be determined based on its

organic carbon normalized partition coefficient, K_{oc} value. A K_{oc} value of 3.1 to 3.5 implies that tetryl will partition in the soil in a manner similar to TNT (K_{oc} = 3.2) and mobility will depend on the organic content of the soil. Field monitoring studies have indicated that the movement of tetryl through soil to groundwater may also be influenced by other factors such as soil pH (Kayser and Burlinson 1988, Hazardous Substance Data Bank (HSDB) 2001). Because tetryl is subject to photolysis in water, it may also be susceptible to photolysis on sunlit soil surfaces (HSDB 2001).

In general, there is much less published research on fate and transport processes of RDX and HMX than for TNT and the nitroaromatic munitions. Although RDX is less water-soluble than TNT, it also has a lower soil adsorption potential, which leads to an even greater potential for migration to, and contamination of, groundwater. Jenkins et al. (2001) and Pennington et al. (2001, 2002) reported RDX-contaminated groundwater from several of the sites they tested, confirming the transport potential of RDX into groundwater. HMX is only slightly soluble in water and has low volatility. It can be found attached to dust and other particulates in air. However, HMX doesn't bind to soil and sediments so it is likely to move from soil into groundwater, particularly from sandy soils. In general, the HMX adsorption coefficients (K_d) were <1 L/kg in aquifer soils, and within the range of 1 to 18 L/kg in surface soils. In column studies, HMX sorption was approximately described using a linear equilibrium model (Myers et al. 1998). HMX is less sorbed and more mobile than is TNT (Townsend and Myers, 1996; Price et al., 1998). Photolysis is a significant transformation pathway for HMX. A $t_{½}$ of 1.4 to 70 days has been reported, depending on the aqueous media studied. Aerobic degradation appears to be negligible. Dubois and Baytos (1991) examined the long term weathering of soil contaminated with HMX over 20 years, and estimated a degradation half-life in soil of 39 years.

No laboratory information was found on the sorption of nitrocellulose in soils. However, it is reasonable that because of its large molecular size, nitrocellulose is not easily transported through soil. The molecular weight of a polymerized unit with a nitrogen substitution level of 12% is between 70,000 and 100,000 Da (Miles, 1955; Kohler and Meyer, 1993). While sorption coefficients were not found for PETN, its soil transport properties can be deduced from its organic carbon normalized partition

coefficient (K*oc*). The K*oc* and K*ow* values of PETN (Table 2), suggest that it is much less soluble in water and more likely to adsorb to soils than other munition constituents.

Toxicity

TNT is a Class C human carcinogen, considered to be both mutagenic and carcinogenic (Agency for Toxic Substances and Disease Registry (ATSDR)-TNT, 1995). The DNT's are classified as possibly carcinogenic to humans (ATSDR-DNT, 1998) and are known carcinogens of laboratory animals. Exposure to both 2,4- and 2,6-DNT effects the central nervous system, the cardiovascular system and the blood, resulting in formation of methaemoglobin. The 2, 4-DNT isomer is considered to be very toxic to aquatic organisms. The likelihood of tetryl to be a carcinogen or mutagen is unknown (ATSDR 1999).

The classification of RDX as a Class C carcinogen (possible human) has been primarily based on research with mice (US EPA-IRIS-RDX, 1998a). HMX is classified as a Group D carcinogen (not classifiable) because no cancer bioassays, epidemiological studies, human studies, or chronic animal studies are available (US EPA-IRIS-HMX, 1998b). RDX is less toxic to human and environmental health than TNT, but more toxic than HMX. HMX environmental and health effects are largely unknown.

The environmental effects of PETN are unknown. Human health effects are primarily from exposure of eyes, skin and respiratory system to PETN dust particles. Prolonged exposure can lead to death from asphyxiation or pulmonary edema. PETN hasn't been investigated for carcinogenic and/or mutagenic potential.

Processes Significant to Range Management of HE

Understanding that many of the HE components are considered as contaminants with potential negative health effects on humans and that the use of these materials is critical for providing the US military with the most effective munitions to perform a number of critical tasks, sustainable use of these compounds on test and training ranges is an important goal from both a conservation and tactical standpoint. Optimal technologies suitable for successful and ensuring sustainable use of energetics on active ranges will be inexpensive, easily applied in remote locations, effective on heterogeneous contaminant distributions, effective over wide areas, effective on multiple energetic compounds, non-intrusive (to the extent possible), and able to be incorporated into normal range

operations. While containment of the compounds of concern that prevents the transport of contaminants towards ground and surface waters is a goal; ultimately, technologies that completely degrade the chemical to environmentally benign end products inexpensively and without disrupting range activities is attractive. Such a technology will reduce the costs associated with the eventual range closure.

This review focuses on technologies that are in demonstration-phase and others that are in the investigative-phase. It concludes with a brief examination of the future technologies that may be deployed to degrade explosive contamination in soil, prevent its migration to ground and surface waters, and ensure sustainable use of military training and testing ranges.

II. State of the Science and Engineering

An examination of the SERDP website finds at least five plant-based research projects due to be completed in FY07 to FY11 and only one or two chemical treatment investigations. Two field projects are listed on the ESTCP web-site as being completed and verified, both applying to groundwater. These are “Monitored Natural Attenuation of Explosives in Groundwater (ER-9518)” and Phytoremediation of Explosives-Contaminated Groundwater in Constructed Wetlands (ER-9520)”. The monitored natural attenuation (MNA) project was successful in that the mass of contaminant in the groundwater was reduced at reduced cost. The drawback is the length of time required for treatment (an estimated 20 years at the study site, LAAP). MNA is an alternative at sites for example, where an ecologically sensitive habitat is involved and treatment time is not an issue. The field demonstration of the constructed wetlands compared a two-cell lagoon-based wetland containing submergent plants to a two-celled gravel-based wetland planted with emergent wetland plants. This project was completed in 1999, with mixed results. The lagoon-based wetland was unable to meet treatment standards for RDX and HMX and was only able to treat TNT effectively during the initial startup phase. The gravel-based wetlands were more successful, but were adversely affected by cold weather. A third field study has been completed (FY07) although not yet listed on the website. This is ER-0110 “Biologically Active Zone Enhancement (BAZE) for In Situ RDX Degradation in Ground Water” conducted at NOP. This field study of sequential

reductive transformation of RDX in groundwater was successful and could be implemented at suitable sites. No completed and verified field projects have been listed for explosives treatment/containment in training range soils although several projects are due to be completed in the coming FY.

In addition to the SERDP and ESTCP research studies, the National Research Council (NRC 1999), Rodgers and Bunce (2001) and the Federal Remediation Technologies Roundtable (FRTR, 2006) have reviewed many of the current technologies available for the treatment of explosives-contaminated soil and groundwater. The FRTR also supplies case studies and cost and performance reports when these technologies have been field-tested. The largest drawback is that most of these processes have been developed and tested only with TNT. The performance of the technology with other explosives, metabolites, and/or mixed explosive compositions is often unknown.

Although several systems are being developed commercially, basically current energetics management of soil consists of excavation and relocation of the material in an off-site hazardous waste storage facility. Groundwater management consists of setting up a variation of a pump-and-treat system. In summary, there are no available technologies that can effectively remediate or prevent the wide range of type, concentration, and distribution of energetic contamination currently found on active training ranges. There is also no available technology to prevent transport of the explosives into the groundwater.

III. Summary of Technical Findings and Issues

Current Research in Demonstration Phase

1. Base Hydrolysis

Alkaline hydrolysis technologies provide promise for long-term sustainable use based on the susceptibility of the nitroaromatic and nitrate ester molecular structures to nucleophilic attack and subsequent transformation (Urbanski, 1964). A significant background of data has now been established for the alkaline hydrolysis of nitroaromatic, nitramine and nitrate ester energetic compounds: Arienzo (1999), Balakrishnan et al. (2003), Croce and Okamoto (1979), Davis et al. (2006, 2007, unpublished data), Emmrich (1999, 2001), Epstein and Winkler (1951), Felt et al. (2001a and b, 2002), Garg

et al. (1991), Hansen et al. (2001), Heilmann et al. (1994), Heilmann et al., (1996), Hoffsomer and Rosen, (1973), Hoffsommer et al. (1977), HSDB 2001, Huang et al. (2005, 2006), Kayser and Burlinson 1988, Saupe et al. (1997), Saupe and Wiesmann (1996), Wu, 2001. The nitroaromatic compounds degrade the most rapidly, however the half-life for both TNT and RDX at pH >10.5 in soil has been determined to be < 1 day. Tetryl at pH 11.5 has a half-life in water of just minutes, nitrocellulose, approximately 3 hours (Davis et al. unpublished data). The nitramines break down more slowly. HMX is degraded at a slower rate than the RDX, but this rate increases with increasing pH (Balakrishnan et al. 2003, Davis et al. 2006). The end products of base hydrolysis of energetic compounds when conducted at a pH of 10.5 and higher are nitrite (NO_2), nitrous oxide (N_2O), nitrogen (N_2), ammonia (NH_3), formaldehyde (HCHO), formic acid (HCOOH), carbon dioxide (CO_2), all non-toxic, environmentally benign compounds.

The information gained from these bench- and pilot-scale experiments has been scaled-up and is currently being demonstrated on hand grenade ranges at Ft. Jackson and West Point (ER-0216) with completion of field testing anticipated in FY08. The results up to this point have demonstrated that topical application of lime to the grenade ranges is a cost-effective and long-term management strategy to degrade existing energetic materials and prevent their migration to the groundwater. RDX was reduced by over 50% in soils that were in training use (>54,000 grenades/yr) after liming (Table 3). Also note that the pre-lime RDX concentration at the second lime treatment was very low and had continued to decrease from its post-liming concentration. RDX concentration in pore water was sampled in the field using a number of suction lysimeters set up surrounding the control and treatment throwing bays. The results (Figure 2) demonstrate a clear reduction in the mass of RDX in pore water from the limed bay.

Table 3. Field demonstration results from Ft. Jackson, SC of RDX in limed and unlimed hand grenade range soil.

Sampling Date	Bay 4 (Limed) Avg RDX Conc. (ppm)			Rain Between Sample Events (inches)	Post Lime % Soil Moisture
	Pre Lime	Post Lime	% Change		
Apr 06	4.21	<1.75[1]	>58%	0.12	2.21
Oct 06[2]	0.42	<0.08	>59%	3.2	6.36
Jan 07	<0.09	<0.10	No Change	0	6.83

1 Report limit (0.02 ppm) used in calculations where '<' present.

2 Pre-lime samples taken in Jul; approximately 30 days between liming and post liming samples.

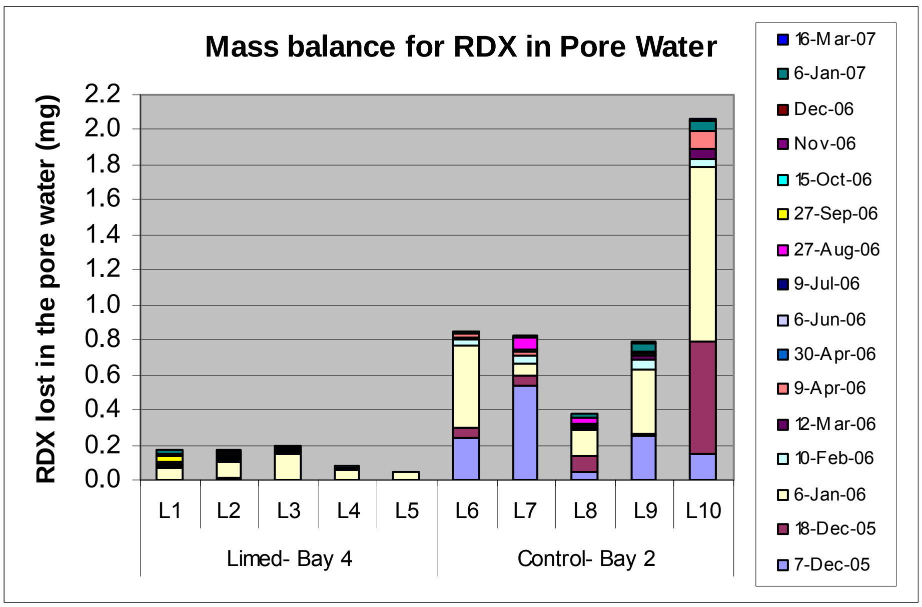

Figure 2. Field demonstration results from Ft. Jackson, SC of RDX in pore water from limed and unlimed hand grenade range bays.

2. Near-Surface Biological Transformation

There are several biologically-based treatment strategies currently under demonstration. These technologies incorporate an organic substrate into either a soil amendment or, for groundwater, a barrier wall. The soil amendment (ER-0434) technology uses peat moss, as a long-lived, high-capacity sorbent, and soybean oil, for its

properties as a slow-release microbial stimulant. When applied to the soil surface the combination is expected reduce the concentration of HE residues in the soil and the underlying groundwater. Early reports published by this group indicated that a 1-in layer of this treatment applied to the soil surface reduced the flux of new HE residue to the subsurface by more than 70%, compared to an untreated control. The technology is expected to be of greatest use at installations where the dominant soil type is sand, which receive moderate to high amounts of rainfall, and where the residues are concentrated in small, easily-managed areas. The demonstration is being conducted at Ft. Jackson, SC, by Shaw Environmental and has an anticipated completion date of 2007. The permeable reaction barrier (PRB) groundwater treatment (ER-0426) uses organic mulch as an electron-donor to promote biological reduction of the energetic compounds. The anticipated completion date for this project is 2008.

3. Barrier wall systems – chemical and electrical

Other PRB systems in demonstration that rely on chemical transformation of the energetics rather than biological transformation include zero-valent iron (ZVI) and electricity. Both projects have an anticipated completion date of 2007. The e-barrier system is actually a panel of closely spaced permeable electrodes inserted into the ground in a permeable reactive barrier format. This demonstration has been conducted at Pueblo Chemical Depot as ER-0519.

4. Phytoremediation

Phyto-treatment has been successfully applied to groundwater remediation of chlorinated solvents, pesticides and explosive compounds by Dr. Jerald Schnoor (in ESTCP Project CU-9519 and others). The primary disadvantage of the system using short rotation woody crops, as stated in the Demonstration results for CU-9519, was the length of time required for the trees to impact the groundwater flow and the solvent mass. Modeling effects past the designated study period indicated an increase in biodegradation of the TCE across the plume after the first three years of the phyto-treatment. In support of phytoremediation, research on the uptake of explosive compounds TNT, RDX, and

HMX into plants has elucidated new pathways for storage and metabolism of these compounds (SERDP project CU-1317).

The applicability of phytoremediation to sustainable use of HE is also being explored in a demonstration project directed toward reducing residual concentrations of energetics in the plant root zone and vadose zone pore water. Phytoremediation in the root zone will also employ techniques of biostimulation to enhance the aerobic and anaerobic biodegradation of the HE (ER-0631, anticipated completion date – 2008). This demonstration is being conducted in Hawaii and focuses on tropical plants and soils. It is expected to be most useful at tropical installations with shallow soils.

Under the auspices of the Army's Environmental Quality and Technology Program, Distributed Sources Focus Area (Remediation Management of Distributed Sources of Munitions Constituents on Ranges), 18 phytoremediation studies have been completed. Two of these completed studies are lysimeter studies to evaluate the effect of plants on soil degradation, runoff and leachate concentrations of explosives, and an evaluation of plant treatments for propellants (DNT, NG, and perchlorate) in soil. The lysimeter studies showed a significant increase in the amount of RDX degraded in planted soils (Figure 3).

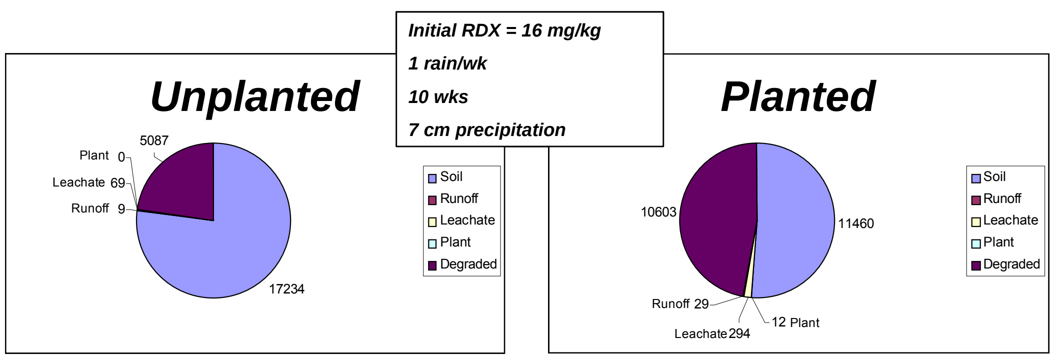

Figure 3. The results of RDX phytotransformation on a laboratory lysimeter scale.

Earlier studies performed in the Remediation Management of Distributed Sources of Munitions Constituents on Ranges program indicated enhanced removal of propellants in hydroponic reactors. Soil degradation studies were conducted using yellow nutsedge – YNS (*Cyperus esculentus*) (YNS) and Indian Grass -Ind. Grass (Sorghastrum *nutans*). They removed nearly 90% of DNT, while no removal was found for the control. The

difference was more modest for perchlorate, about 60% removal compared to about 40% for the control. No difference was found for the nitroglycerine (Figure 4).

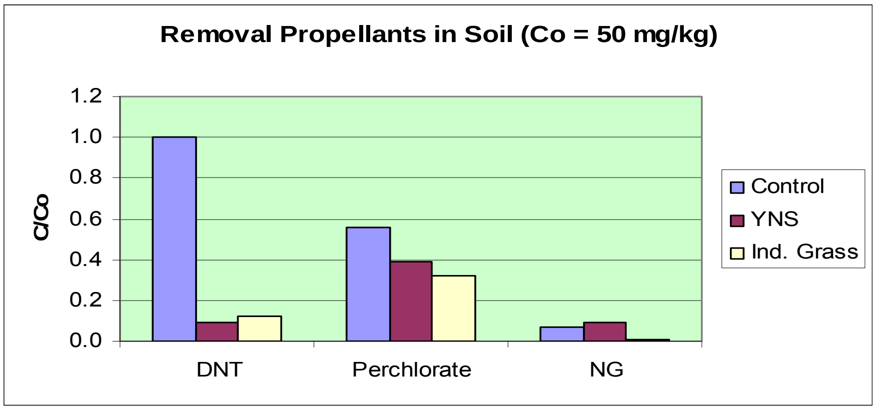

Figure 4. Removal of propellants from soil by yellow nutsedge and Indian rye grass.

Chemical treatment in combination with phytoremediation was also shown to be a successful approach (Figure 5). Grass growth was healthy even at a 5% lime addition and may provide a means of erosion control/soil stabilization in conjunction with the explosives degradation resulting from base hydrolysis.

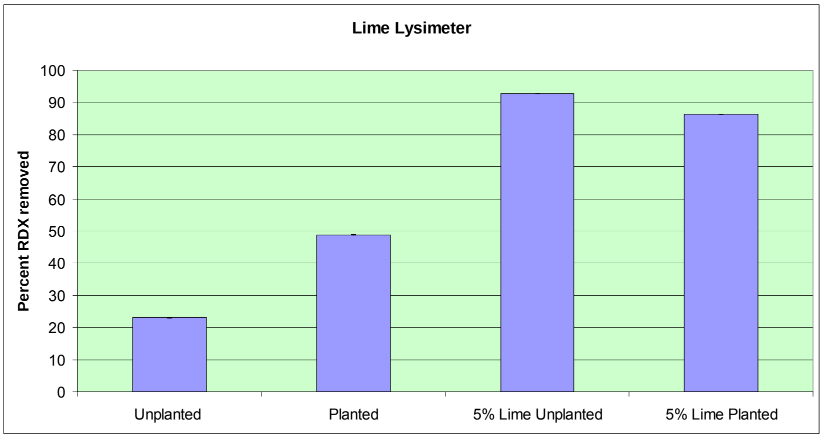

Figure 5. Lime treatment used in conjunction with phytoremediation.

The Remediation Management of Distributed Sources of Munitions Constituents on Ranges program also included the investigation of the use of common and native grasses to provide both explosives degradation and soil stabilization/erosion prevention. The mechanism of removal examined was enhanced microbial biodegradation in the root zone. The root exudates significantly increased biodegradation of TNT and RDX. From

pot and lysimeter studies, the plantings resulted in general decreases in explosives migration, in most cases.

Current Research in Investigative Phase

1. Phytoremediation

A number of plant-based research projects for treatment of energetics-contaminated groundwater and soil are on-going. A project that involves engineering transgenic grasses that will uptake and degrade RDX and TNT, as well as withstand drought and disruption by live-fire ammunition and heavy equipment, is scheduled for completion by 2011 (ER-1498).

There are four studies currently underway as part of the Remediation Management of Distributed Sources of Munitions Constituents on Ranges Program; a large-scale lysimeter study, an allied bench-top study and a microbial population study looking at the effect of plants that are degrading explosives on rhizosphere properties.

2. Open Burning

The project "Impacts of Fire Ecology Range Management (FERM) on the Fate and Transport of Energetic Materials on Testing and Training Ranges" was funded by SERDP (CP-1305) and the final report published in 2006. Fire ecology is the science of using fire to manage vegetation and ecosystems. Fire Ecology Range Management (FERM) combines fire ecology and phytoremediation into an easily implementable and innovative approach for addressing explosives residual contamination on ranges by applying principles of fire ecology to develop range management techniques that will minimize the problems associated with explosive residues.

Fires in target areas are relatively common occurrences. Dry grass in target areas can ignite as a result of detonations, but standard practice is to quickly suppress these fires. Explosive compounds including TNT and RDX are unstable at high temperature and are amenable to thermal decomposition. Fires have the potential to destroy energetic compounds which are either associated with the plants that are burned or are in or on the surface soils which are heated by the burn. Combining the technologies controls the migration of explosives compounds in/from surface soils and thermally destroys the

residuals before they reach groundwater or are transported from the site during surface runoff events.

The overall conclusion from the FERM investigation was that using prescribed burning on ranges has potential for destroying a significant amount of explosives residual in surface soils and in and on plant tissues.. It is anticipated that FERM would be a component of a multi-component program for managing explosives residuals resulting from testing and training operations on ranges.

3. Retention ponds

The applicability of phytoremediation to sustainable use of HE has been explored in studies incorporating engineered wetlands for the simultaneous impoundment of contaminated surface and wastewaters and degradation of the explosives. This successful study was conducted at Iowa Army Ammunition Plant (IAAP). The low-cost, non-labor-intensive treatment reduced RDX concentrations to below the discharge requirement of 2 ppb in two years of treatment. Although concentrations rose slightly each year during the non-growing season, they never increased to initial levels (Kiker et al., 2000).

The use of retention ponds for collection of surface water prior to migration off-site is not a technology that has been directly researched to a large extent for HE control on ranges. There has use of these devices and the associated water directing structures at army ammunition plants (IAAP), open burn open detonation areas (Crane, IN), small arms firing ranges, and catch boxes. Coupling of these techniques with phytoremediation/bioremediation in both designed and fortuitous situations has been shown to be effective at reducing surface water explosives' concentrations bellow regulatory limits for release (Iowa AAP and Crane, IN). These types of technologies are most applicable to areas where the HE use is highly localized, the concentration of the compounds of concern are high in the surface water leaving the localized area is high, and where the point of compliance is relatively near the area of use.

IV. Future Research and Technology Needs

While a number of technologies have been demonstrated to be effective at reducing or eliminating the organic compounds associated with high explosive containing

munitions, the sustainable range where negligible contaminant migration via surface or ground water is not currently possible. The Department of Defense performs live fire training in a wide range of environments. Variations in soil type, climate, frequency of range use, and type of munitions used across the vista of DoD training facilities negate a simple answer to this complex environmental engineering problem.

The key to successful implementation of systems for performing negligible environmental impact training with regards to high explosives is simplicity of use. The solutions must be easily applied and have minimal impact on the true purpose of live fire training facilities which is familiarization in a realistic use setting. To that end it is expected that future systems will incorporate advances in the areas of advanced materials, low cost-real time sensing, and robotics coupled with the knowledge gained in the development of the current suite of environmental engineered solutions.

V. Conclusions and Recommendations

The types of testing and training activities that the DoD uses covers a wide range of munitions and geographies. These training and testing conditions are constantly undergoing changes with training scenarios phasing in and out based on specific geopolitical conditions and the enhanced or novel capabilities of new munitions. The result of this from and environmental engineering research standpoint is that there will be no simple solution to the complex set of issues associated with sustainable use of HE in this non-static field. No single technology is expected to be applicable in all environments that will ensure sustainable use of HE.

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14. ABSTRACT
The sustainability of the Department of Defense's (DoD) operational ranges is crucial to maintaining the readiness of the military forces and developing and testing improved weapon systems. SERDP and ESTCP convened a Technical Exchange Meeting on DoD Operational Range Assessment and Management Approaches in August 2007 to (1) inform representatives from the range management and assessment communities of applicable technologies developed by SERDP, ESTCP, and the Army Environmental Quality Technology Program and (2) identify technology needs of the range management and assessment community that could be addressed through additional research and development efforts. Two breakout sessions facilitated discussions of the current state of the science and identified data gaps that could be addressed through additional research, development, testing, and evaluation (RDT&E) activities. Specific research paths and demonstrations were identified and prioritized.

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